

The Standardization of Volumetric Solutions

By

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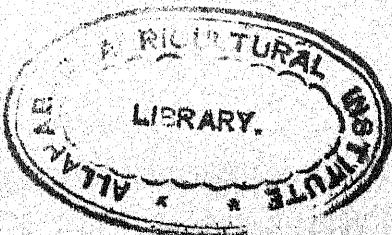
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Foreword

ORDINARILY, a standardized solution is a means to an end and not the end itself. Therefore, a set of good methods for preparing such solutions is very welcome. Analysts, research and other laboratory men have had training in these methods but when they wish to make up a solution, they do not like to spend much time in going through books and journals in order to find the directions for making up the specific one desired. In this book, the author has gathered together methods which have stood the test of laboratory experience, and has described them in a concise manner all ready for rapid laboratory use.

This book is not for the beginner, since it presupposes a general knowledge and practice of analytical chemistry. It is a handy reference work for the man who must hurry to get his results. The discussions of the methods and their good and bad points are short and very useful, and the text is replete with helpful hints, equations, tables of important data, expressions for calculating normalities, etc.

The writer believes that his friend and former asso-



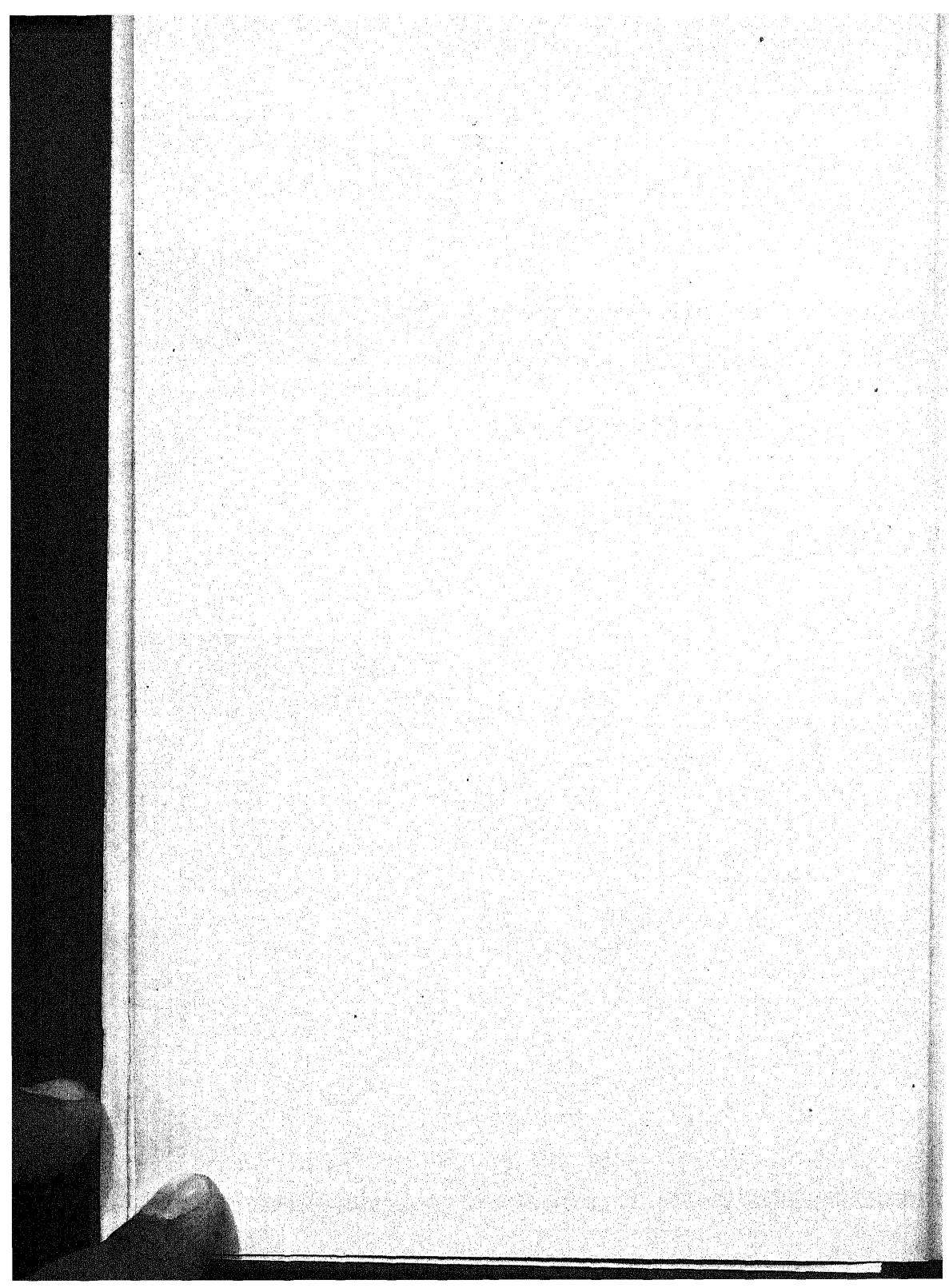
ciate has done his self-appointed task well. His long experience in his chosen field gives him the proper background for such a work and this compilation of good practical methods ought to be of real service.

HARRY L. FISHER

Acknowledgment

THE author wishes to express his thanks to Dr. Harry L. Fisher, U. S. Industrial Alcohol Co., V. L. Burger, General Laboratories, United States Rubber Products Co., and J. B. Lewis, Esso Laboratories, Standard Oil Co. of New Jersey, all of whom contributed helpful criticisms and suggestions.

R. B. BRADSTREET



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CHAPTER I

General Consideration: Definition of a Normal Solution.

Normality and Equivalent Weight. Effect of Temperature and Buoyancy Error. Requirements for Standard Solutions. Calculations. Requirements of an Indicator.

A NORMAL solution may be defined as a solution of known concentration, a liter of which is equivalent to a gram-atom of hydrogen. A fractional normal solution contains a fractional gram-atom of hydrogen per liter. The equivalent weight is the weight in grams corresponding to one gram-atom of hydrogen. In acid-base reactions, the hydrogen equivalent is easily found, since it is the number of titratable hydrogen atoms, thus:

- (1) $\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$
- (2) $2\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
- (3) $\text{Ca}(\text{OH})_2 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$
- (4) $3\text{NaOH} + \text{H}_3\text{PO}_4 \longrightarrow \text{Na}_3\text{PO}_4 + 3\text{H}_2\text{O}$

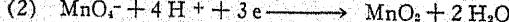
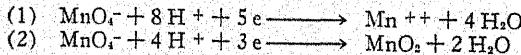
The equivalent weight of either NaOH or HCl in (1) is the mol weight, that is, one mol of NaOH is equivalent to one mol of HCl. In (2), two mols of NaOH are equivalent to one mol of H_2SO_4 , and the

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equivalent weight of H_2SO_4 will be the molecular weight divided by 2, since the number of replaceable hydrogen atoms is 2, and a normal solution will contain this weight of H_2SO_4 in a liter of water. Equation (3) shows that 2 HCl are equivalent to 1 $\text{Ca}(\text{OH})_2$. Calcium hydroxide is dibasic, and therefore has the equivalent of two replaceable hydrogens. Hence, the equivalent reacting weight will be the molecular weight divided by two. In case (4), by inspection it will be seen that there will be three replaceable hydrogen atoms (if all are titrated) and that the equivalent reacting weight will be the molecular weight divided by three.

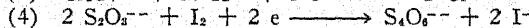
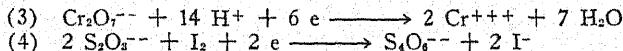
In dealing with oxidation-reduction equations, the reacting weight (or equivalent weight) of a substance is the weight of substance equivalent to one half mol of oxygen (one half mol of oxygen is equivalent to one mol of hydrogen). Since oxidation-reduction is really electron transfer, it is simpler to determine the change of valence from the equation involved. The molecular weight divided by the change in valence is the equivalent reacting weight, and this weight made up to one liter is equivalent to one gram atom of hydrogen, or one half gram atom of oxygen.

This may be illustrated more clearly, perhaps, by the following examples:



In the first equation, manganese, as a permanganate, with a valence of 7, has been reduced to a manganous salt having a valence of 2, or, in other words, there has been a transfer of 5 electrons. This reaction takes place in acid solution and the equivalent weight, therefore, is $\frac{\text{MnO}_4^-}{5}$.

Equation (2) represents oxidation with alkaline permanganate, and by inspection it is found that the valence change is 3. Consequently, there has been an electron transfer of 3, and the equivalent weight is $\frac{\text{MnO}_4^-}{3}$.



Example (3) illustrates dichromate oxidation, which involves a transfer of 6 electrons, and gives a reacting weight equal to $\frac{\text{Cr}_2\text{O}_7^{2-}}{6}$. In the last equation (4), the iodine has been reduced from zero valence to a valence of minus 1, and therefore, the equivalent weight will be $\frac{1}{1}$.

Since oxidation is the result of a loss of electrons, and reduction represents a gain of electrons, it is not necessarily true that an oxidizing agent always contains oxygen [as for instance iodine in equation (4)]. Equations (1) and (2) show that the equivalent reacting weight of an oxidizing agent may vary depending upon the medium in which the reaction takes place.

The equivalent weights of precipitation reagents may

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be likewise determined from their reactions. For instance:



By inspection, it is seen that one mol of silver nitrate reacts with one mol of sodium chloride to form one mol of silver chloride. Therefore, their equivalent reacting weights in this case are their molecular weights.

Standard solutions, in some cases, may be prepared without further standardization where the substance is known to be pure, and does not change appreciably due to atmospheric conditions. Potassium dichromate, potassium iodate, oxalic acid, and silver nitrate are a few examples. However, it is always desirable to standardize a solution. It is good practice to weigh the substance as accurately as possible, to avoid the necessity later of diluting to the proper normality. Also, it is advisable to weigh slightly more than the theoretical amount, since it is easier to dilute than to raise to the desired normality. The dilution may be calculated as follows (contraction of the solution being neglected, as usually no great error is involved):

Let V = volume of solution before dilution

V_1 = volume of solution after dilution

N = normality of solution before dilution

N_1 = normality desired after dilution

Then $NV = N_1V_1$

NV

or $V_1 = \frac{NV}{N_1}$

and $V_1 - V = x \text{ cc of solvent to be added to}$
 $\text{the original volume.}$

Solutions as dilute as tenth normal are affected but little by temperature changes,^{1, 2, 3} but with half normal and normal solutions, the temperature should be considered. The following table, after W. Schloesser,² gives a partial list of corrections to be applied to standard solutions referred to 20° C as a standard temperature.

T°C	Water		0.5N HCl	1.0N HCl	0.5N NaOH	1.0N NaOH
	0.01N Solutions	0.1N Solutions				
	0.1N HCl					
15	+0.8	+0.9	+0.9	+1.0	+1.1	+1.3
16	0.6	0.7	0.8	0.8	0.9	1.1
17	0.5	0.6	0.6	0.6	0.7	0.8
18	0.3	0.4	0.4	0.4	0.5	0.6
19	0.2	0.2	0.2	0.2	0.2	0.3
20	0.0	0.0	0.0	0.0	0.0	0.0
21	-0.2	-0.2	-0.2	-0.2	-0.2	-0.3
22	0.4	0.4	0.4	0.5	0.5	0.6
23	0.6	0.6	0.7	0.7	0.8	0.9
24	0.8	0.9	0.9	1.0	1.0	1.2
25	1.0	1.1	1.1	1.2	1.3	1.5

Schloesser assumes the coefficient of cubical expansion of glass to be 0.000027.

Certain precautions should be observed regarding standard solutions. It is good policy to store all standard solutions in the dark, where there is a minimum of temperature variation, and where the containers cannot be contaminated with dust or organic material. Solutions should be labelled in the following manner:

¹ Yokichi Osaka, *J. Tokyo Chem. Soc.* 40, 424 (1919); *Chemical Abstracts* 14, 159 (1920).

² W. Schloesser, *Chem. Ztg.* 29, 510 (1905).

³ N. Schoorl, *Chem. Weekblad* 23, 581 (1926).

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Name and formula

Normality or factor

Name and notebook reference of the person
making up and standardizing the solution

Temperature of standardization

Date of standardization

This information makes it easier to check any possible errors in standardization. It is also advisable to record the equivalent weight, to facilitate preparation of subsequent solutions. Solutions that have stood for a considerable time,⁴ and particularly those that show a tendency to deteriorate quickly, should always be re-standardized before using.

Usually, in the preparation of standard solutions, the theoretical amount of substance is weighed in air against brass weights, neglecting the effect of buoyancy. Since atomic weights and, it follows, molecular weights are calculated to *vacuo*, there is, therefore, an error introduced when weighings are made in air. The magnitude of this error is such that it may be neglected. The equivalent weights found in the following pages are not corrected to *vacuo*.

Archimedes' principle states that bodies immersed in a fluid are buoyed up by a force equal to the weight of the displaced fluid. This law holds for gases as well as for liquids.

⁴ J. Linder, *Mikrochemie*, Festschr. von Hans Molisch, 301-13 (1936).

If a mass of brass is weighed against brass weights, the buoyancy force on both sides of the balance is the same, provided the volume is the same, and no correction need be made. If, however, the density of the weights is greater than that of the substance being weighed, the apparent weight of the substance in air will be less than its true weight in vacuo. The weight reduced to vacuo may be calculated from the following formula:

$$w = W + W\delta\left(\frac{1}{d} - \frac{1}{d_1}\right)$$

where W = true weight

w = apparent weight in air

δ = density of air

d = density of substance being weighed

d_1 = density of weights used

Density of brass is 8.4, and density of air is 0.0012.

Since the majority of commonly used standard solutions cannot be prepared by direct weighing of the substance in question, some means must be taken to establish the exact value of the solution. Any errors in standardization will be recurrent in all subsequent determinations made with the solution. In the first place, therefore, some substance of known purity must be available for evaluating the solution. Certain requirements are necessary for a primary standard. It should have a high equivalent weight, be easily obtainable pure, or easily purified. It should be neither hygroscopic nor efflorescent.

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It is obvious that the primary substance must bear a stoichiometrical relation to the standard solution.

In the actual standardization, several other points must be observed. In weighing out the primary standard, it must be remembered that, in general, the accuracy of an analytical balance is ± 0.1 mg, so that sufficient sample must be weighed to reduce this error to a minimum. This, in effect, is an argument for the use of substances having a high equivalent weight. The actual titration should fall within the limits of the burette, that is, it should not titrate over 50 cc. No less than 40 cc should be used. The errors involved in titration, while small, are cumulative, (reading, drainage, and error in the end point—plus or minus one drop). If the end point is overrun, say, by one drop, then the error involved here is about ± 0.03 cc, since this is approximately the volume of one drop from a fine-tipped burette. If, now, the remaining errors of reading and drainage are added to this, it is easily seen that at least 40 cc must be used in order to keep the errors within 0.1–0.2 per cent. Since the accuracy of standardization is between 0.1 and 0.2 per cent, it will be understandable that every precaution must be taken. Standardizations, involving a back titration with another standard solution, are open to further errors which may be additive, since they involve an additional titration. At least three checks should be made on any standardization. They should check within 0.2 per cent. Care-

fulness cannot be too highly stressed in the standardization of a reagent, since the accuracy of future determinations depends upon the accuracy with which the value of the standard solution was determined.

The calculations involved in volumetric standardizations are very simple. Normality may be calculated according to the following formula.

$$\text{Normality} = \frac{\text{weight of standard substance}}{\text{milliequivalent of std.} \times \text{cc titration}}$$

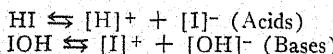
The milliequivalent may be defined as the weight of standard substance contained in one cubic centimeter of a normal solution of that standard substance. The milliequivalent multiplied by the number of cubic centimeters used for titration gives the weight in grams of standard substance. The weight of standard substance divided by this gives the ratio of the standard solution to the theoretical normal solution. In other words, if the normality found is 0.1050 normal, it means simply that one cubic centimeter of the solution contains 1.050 times as much as the theoretical amount.

In the choice of a suitable indicator, the field is so large that it may, in many cases, be left to the discretion of the operator. There are, however, certain requirements to be met, namely, an indicator whose transition range is within the range of the reaction involved, and a color change which is sharp enough to be differentiated by the analyst.

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The point at which the indicator changes color is taken as the end point, meaning that at this point, an equivalent amount of standard reagent has been added. Strictly speaking, this may or may not be the exact end point or equivalence point. This can be determined by electrometric titration, the difference in the two titrations being known as the titration error.

Most indicators are organic, and are either weak acids or weak bases. They are slightly ionized, according to the following:



Oxidation and reduction indicators depend for their color changes on oxidation or reduction of themselves. In some cases, the reagent itself acts as its own indicator.

A recent class of indicators, known as adsorption indicators,⁵ has been used with more or less success in the determination of halides and sulphates. In general, they are not applicable to standardizations, although they have been used⁶ in acidimetry and alkalimetry. A theoretical discussion of various types of indicators will be found in Kolthoff and Furman, *Volumetric Analysis*, Vol. I (1928), 82.

⁵ A. R. Ubbelohde, *Chem. Rev.* 16, 53 (1935).

⁶ Sachindra Nath Roy, *J. Indian Chem. Soc.* 14, 120 (1937); see also *Chemical Abstracts* 31, 5293 (1937); *Chemical Abstracts* 30, 8064 (1936).

CHAPTER II

Calibration of Volumetric Apparatus

SINCE volumetric procedures require accurate measurement of volume, the importance of knowing the exact volumes of the various apparatus used cannot be overlooked. The simplest and most obvious solution to this problem, wherever possible, is to use apparatus calibrated by the U. S. Bureau of Standards. Apparatus calibrated by the Bureau is always accompanied by a table of volume corrections over a range of working temperatures. This, however, is comparatively expensive, and it is easy enough to purchase a good grade of glassware that falls within the limits of tolerance allowed by the Bureau of Standards, and calibrate it in the laboratory. It is never advisable to rely on the accuracy of a piece of apparatus without first calibrating it.¹

In the process of standardization, volumetric flasks, pipettes, and burettes are necessary. Volumetric flasks are graduated to *contain* a definite volume, and pipettes

¹ *Bur. Standards Circ. No. 9* (1916).

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and burettes to *deliver* a definite volume. Before any attempt is made to calibrate apparatus, it must be thoroughly cleaned. This is done by rinsing with tap water, filling with fresh chromic acid, and letting stand for several hours. After this treatment, the chromic acid is withdrawn, and the apparatus washed free from the acid with tap water. It is now washed with distilled water and drained. If the water does not appear to wet the inside of the apparatus evenly, several washes with acetone, and then distilled water may be efficacious. If this does not have any effect, another treatment with chromic acid will be necessary.

Since the calibration is made with water, it is not necessary to dry the apparatus. All volumetric apparatus are calibrated to contain or deliver a definite volume at a standard temperature, usually taken at 20° C. This means, of course, that at this temperature, the apparatus will contain the designated volume. At any other temperature, the volume will vary depending upon the expansion of the glass and the density of water. Buoyancy effect is also taken into consideration, using 0.0012 gm per cc, the density of air (not strictly correct, because this figure will vary slightly depending upon temperature, humidity and pressure), as sufficiently accurate for all calibrations.

Usually, the temperature at the time of calibration is not 20° C, so that all weighings are made under existing conditions and referred back to 20° C. The

liter is the unit of volume in the metric system, and is the volume of a mass of one kilogram of water at maximum density.

CALIBRATION OF FLASKS

Fill the flask to the graduation on the neck with distilled water at room temperature and weigh. This weight is reduced to *vacuo* (mass), according to the formula:

$$w = W + W \delta \left(\frac{1}{d} - \frac{1}{d_i} \right) \quad (\text{See Chapter I})$$

The volume at room temperature is this mass divided by the density of water at room temperature.

$$\text{Volume at R. T.} = \frac{\text{Mass}}{d_{\text{H}_2\text{O}}}$$

This gives the volume of the flask at room temperature. It is now necessary to calculate this volume to 20° C, and this may be done by applying the following:

$$V_T = V_{T_1} + 0.000025 V_{T_1} (T - T_1)$$

Where V_T = Volume at standard temperature

V_{T_1} = Volume at calibration temperature

T = Standard Temperature

T_1 = Calibration Temperature

Coefficient of cubical expansion of glass* = 0.000025

* Coefficient of cubical expansion of Pyrex glass is 0.00000032 or less, between 19 and 350° C.

CALIBRATION OF PIPETTES

After cleaning the pipette, immerse the tip in water, fill to the mark, discard and fill again exactly to the graduation. Wipe any excess water from the pipette by means of a soft rag and transfer the contents to a tared and stoppered Erlenmeyer flask, allowing the pipette to remain vertical until discharged and then touching the tip to the side of the flask and allowing it to remain for fifteen seconds. Do not blow out the pipette. Reweigh the Erlenmeyer flask and calculate the volume in the same manner as for volumetric flasks.

CALIBRATION OF BURETTES

The calibration of a burette may be carried out in two ways: 1. Measure 5 cc of water from the burette into a tared and stoppered 100 cc Erlenmeyer flask and weigh. Record the weight. Add 5 cc more to the flask and reweigh. Repeat this process until the capacity of the burette has been measured into the flask and weighed. 2. Measure 5 cc from the burette and weigh. Refill the burette and measure 10 cc into a flask and weigh. Repeat this procedure until the last weighing represents the capacity of the burette. The calculations are the same as for flasks and pipettes. The difference between the true volume and the observed volume is the correction to be applied in a titration. A curve may

be plotted to show the correction and true volume at any point.

When reading the volume, care must be taken to avoid parallax. In the case of pipettes and flasks or any piece of apparatus on which the graduation extends around the circumference, this is avoided, but with burettes, a possible error may occur if the graduation and the eye are not in the same horizontal plane. The error may be either positive or negative. This may be overcome by using a strip of paper having a straight edge, bringing it to the bottom of the meniscus and lining up both sides.

The method of calibration herein described is probably the most common one. Another means of calibration is by the use of Morse-Blalock² bulbs, which, however, require a more complicated set-up, and are generally not available in most analytical laboratories.

² Morse and Blalock, *Am. Chem. J.* 16, 479 (1894).



CHAPTER III

Indicators: Definition, Classification, Classification of Reaction, Acid-Base Indicators, Oxidation-Reduction Indicators, Indicators for Precipitation Reactions. General Discussion.

ANY compound in solution exhibiting a color change or producing a precipitate, by addition of an excess of one of the reactants, may be considered as an indicator. In other words, an indicator produces a visual change at, or near, the equivalence point. It may be a separate compound or one of the reagents, as in the case of permanganate or iodine.

Indicators may be divided roughly into three classes:

1. acid-base
2. oxidation-reduction
3. precipitation

For an extended survey of indicators, and theoretical considerations, reference should be made to the many excellent books on this subject.^{1, 2, 3, 4}

¹ Kolthoff and Furman, *Indicators* (Wiley).

² Kolthoff and Furman, *Volumetric Analysis*, Vol. I & II (Wiley, 1929).

³ Clark, *Determination of Hydrogen Ions* (Williams & Wilkins).

⁴ Hubert T. S. Britton, *Hydrogen Ions* (Van Noststrand).

ACID-BASE INDICATORS

The color change exhibited by indicators is produced by a change in H^+ concentration, and the range through which this occurs is called the transition interval. Most acid-base indicators are weak organic acids or bases which give one color when undissociated (pseudo form) and another when ionized (ionogen). Since they are weak acids or bases, the mass action law applies, and it is obvious, therefore, that the indicator change is a function of the H^+ concentration.

Thus, if $HI \rightleftharpoons [H^+] + [I^-]$

$$\text{then, } K_{\text{Ind.}} = \frac{[H^+] \times [I^-]}{HI}$$

Transposing, $K_{\text{Ind.}} \times HI = [H^+] \times [I^-]$

$$\text{or } \frac{K_{\text{Ind.}}}{[H^+]} = \frac{[I^-]}{HI}, \text{ so that when}$$

$$K_{\text{Ind.}} = [H^+], [I^-] = HI,$$

and the indicator is half changed over. At any pH, then, the equilibrium constant holds, and at any particular instant, there are present both acid and basic phases. At some point, however, either one will be in sufficient concentration to cause a visual change of color.

This change, for the most part, is not sudden, but covers from one to several pH units. This is due,

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mainly, to the inability of the eye to gauge the color change accurately.

The transition range, obviously, has an upper and lower limit, at one end of which, the acid form predominates, whereas the other is alkaline.

If, for instance, 10% of the alkaline form of an indicator is sufficient to produce a visible change in the presence of the acid form, then,

$$\frac{K_{\text{Ind.}}}{[H^+]} = \frac{[I^-]}{HI} = \frac{1}{10}, \text{ and}$$
$$[H^+] = K_{\text{Ind.}} \times 10$$

Expressing this as a logarithmic function,

$$pH = pK_{\text{Ind.}} + 1$$

Now, conversely, if it is assumed that 10% of the acid form is enough to cause a color change in the presence of 90% of the alkaline form, then,

$$\frac{K_{\text{Ind.}}}{[H^+]} = \frac{[I^-]}{HI} = \frac{10}{1}$$
$$\text{or} \quad [H^+] = \frac{K_{\text{Ind.}}}{10}$$
$$\text{or} \quad pH = pK_{\text{Ind.}} - 1$$

The transition interval, therefore, is equivalent to 2 pH units.

The majority of indicators is affected by any great

change in temperature. Salt error, however, may be neglected, unless the concentration is very high. It tends to affect the equilibrium and the color change of the indicator, due to the difference in absorption of light.

A large variety of indicators is available for acid-base titrations, and a suitable choice is dependent upon the classification of the reaction, that is:

1. strong acid-strong base
2. weak acid-strong base
3. strong acid-weak base
4. weak acid-weak base

Each case will be considered separately.

1. Strong acid-strong base. In this case, it may be assumed that both are completely ionized, and if the base is as strongly ionized as the acid, complete neutrality is indicated. Since the definition of a neutral solution is one in which the $[H^+]$ and $[OH^-]$ concentrations are both 10^{-7} , then for this type of neutralization, an indicator having a transition range around pH 7 is acceptable.

2. Weak acid-strong base. If an acid is less strongly ionized than the base used in the titration, equilibrium will be attained in a basic solution. This conclusion is obvious, when it is realized that two conditions must be fulfilled: first, that the ionization constant of the acid must be satisfied, and second, that $C_H \times C_{OH} = 10^{-14}$ (actually 1.2×10^{-14}) will be maintained. At equilib-

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rium, there must be unionized acid present. This lowers the concentration of $[H^+]$ and leaves free $[OH^-]$ in the solution. The pH of the solution, at equilibrium, will be greater than 7, hence, an indicator having a range greater than pH 7 must be used.

3. Strong acid-weak base. If the conditions stated under 2 are reversed, it will be seen that equilibrium will take place in acid solution. In this case, an indicator having a pH of less than 7 should be used.

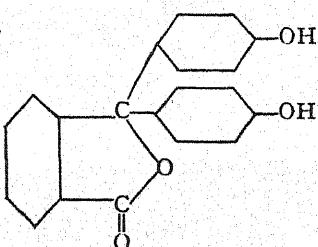
4. Weak acid-weak base. In this case, three equilibrium constants must be satisfied, namely, ionization constants of both acid and base, and ionization constant of the water formed by the reaction. If the acid and base are ionized to about the same degree, e.g. acetic acid and ammonia, then the resulting solution will have a pH of 7. If one is more strongly ionized than the other, the same conditions will exist as stated previously in cases 2 and 3, and the same kind of indicators chosen.

The following represent a few of the indicators most commonly used in acid-base reactions. They cover a wide range of pH.

Phenolphthalein

Type: Belongs to the phthalein group.

Structural formula:

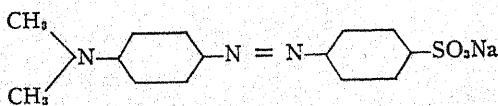


pH range 8.3–10.0. Color change from colorless to red violet.

Methyl Orange (sodium dimethylamino azobenzene sulphonate)

Type: Belongs to the azo group.

Structural formula :



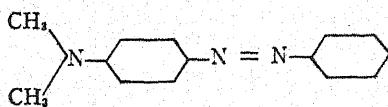
pH range 2.9–4.5. Color change from orange red to orange yellow. Although this indicator is widely used, the color change is not as sharp as could be desired, and it may be replaced, for instance, by methyl yellow. The color change for this indicator is much sharper. Methyl orange is not affected by carbon dioxide.

Methyl Yellow (dimethylamino azobenzene)

Type: Belongs to the azo group.

Structural formula :

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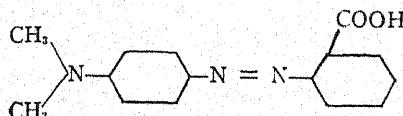


pH range 2.9-4.0. Color change from red to yellow.
(Not affected by CO_2).

Methyl Red (dimethylamino azobenzoic acid)

Type: Belongs to the azo group.

Structural formula:

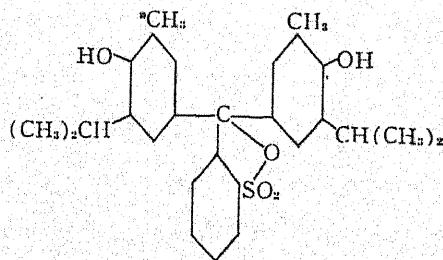


pH range 4.2-6.3. Color change from red to yellow.

Thymol Blue (thymol sulphon phthalein)

Type: Belongs to the phthalein group.

Structural formula:



pH range: Acid 1.2-2.8

alkaline 8.0-9.6.

Color change in the acid range from red to yellow, and yellow to blue in the alkaline range.

OXIDATION-REDUCTION INDICATORS

Any system in which there is a change of valence may be classified as an oxidation-reduction reaction. Therefore, when an atom or complex ion is oxidized, its positive valence is increased, or its negative valence is decreased, and the converse is also true of reduction. In other words, a substance which is oxidized gives up electrons, and a substance which is reduced adds electrons.

Previously, the use of outside indicators was more or less universal for determining the end point. If colorless solutions are to be titrated, it is possible for the reagent to act as its own indicator, for instance, potassium permanganate, ceric sulphate, and iodine.

Internal oxidation-reduction indicators have been applied to dichromate, permanganate, ceric sulphate, and ferrocyanide titrations. An oxidation-reduction indicator should, of course, be reversible, otherwise its use is limited. For every oxidation-reduction equation, there can be calculated a definite electrode potential using the Nernst equation.⁵

$$E = \frac{RT}{nF} \ln \frac{P}{P_0}$$

⁵ Engelder, *Calculations of Qualitative Analysis*, Chapter IX, p. 131.

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which can be simplified to

$$E = \frac{0.059}{n} \log \frac{C}{k}$$

or

$$E = \frac{0.059}{n} \log C + \frac{0.059}{n} \log \frac{1}{k}$$

If the concentration is one molar, then

$$E = \frac{0.059}{n} \log \frac{1}{k}$$

or

$$E = E_o$$

E_o is the oxidation potential at molar concentration and is a constant for each system, so that the oxidation potential may be calculated for any mixture, from the following equation:

$$E = E_o + \frac{0.059}{n} \log \frac{C_{\text{oxd}}}{C_{\text{red}}}$$

where C_{oxd} is the concentration of the oxidized ion, and C_{red} , the concentration of the ion in reduced form.

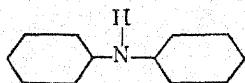
The selection of a suitable indicator is based on the normal potentials of both indicator and the oxidizing-reducing system in question, since the specific action of the indicator is dependent upon its electrode potential. Therefore, any indicator, having a lower oxidation potential than the system in which it is used, will exhibit a color change. There must not, however, be a very

large difference. If this is the case, the oxidation potential (of the system) should be reduced, and this is accomplished in some cases by forming complex ions.

The following indicators have been used successfully in oxidation-reduction reactions.

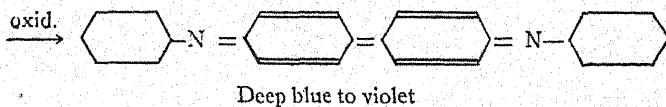
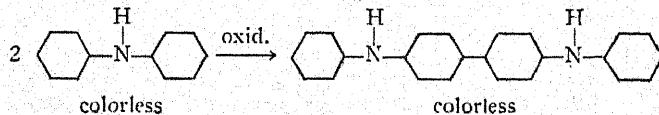
Diphenylamine

Structural formula:



Oxidation potential: -0.76 volts.

The first step in the oxidation of this indicator is to diphenylbenzidine, and thence to colored compound



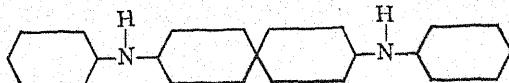
Color change is colorless to deep blue or violet. Since some of the reagent goes to complete the oxidation of the indicator, it is necessary to make a correction⁶ for the amount used.

⁶ W. H. Cone and L. C. Cady, *J. Am. Chem. Soc.* 49, 356 (1927).

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Diphenylbenzidine

Structural formula:

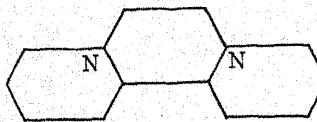


Oxidation potential: -0.76 volts.

Color change is from colorless to deep blue or violet. The oxidation proceeds as above. The blue compound is stable for only a short while in the presence of oxidizing agents.

Ortho-Phenanthroline Complex⁷

Oxidation potential is -1.14 volts. The usual form of this indicator is the ferrous ion complex. The structural formula of *o*-phenanthroline is:



It dissolves in solutions of ferrous salts, three molecules combining with one ferrous ion.

Color change is from red to blue.

Starch Solution^{8, 9}

The preparation of starch solution is more difficult

⁷ *Ortho-phenanthroline*, monograph published by The G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio.

⁸ C. L. Alsb erg and E. P. Griffing, *J. Am. Chem. Soc.* **53**, 1401 (1931).

⁹ C. L. Alsb erg and E. P. Griffing, *J. Am. Chem. Soc.* **48**, 1299 (1926).

than is ordinarily supposed. A solution which will prove satisfactory over a long period can be prepared ¹⁰ in the following manner: Mix 0.5 gm of potato starch with 2.5 cc of water and pour into 200 cc of boiling water, stirring meanwhile. Boil fifteen minutes. Cover the flask or beaker with a watch glass to prevent scum forming by evaporation during boiling. The final solution should not contain any suspended matter. If this is kept covered and allowed to stand on a steam plate, the solution will keep indefinitely. If heating is impossible, 0.25 gm of salicylic acid may be added as a preservative. With this addition, starch solutions have given good end points after a year, although considerable sediment had formed, and only the supernatant liquid was used.

The condition of starch, as received from supply houses, is somewhat uncertain. Sometimes fresh starch contains dextrin, which gives a reddish violet color, and is not immediately discharged by thiosulphate. Starch of this sort should be discarded. The color change is from colorless to blue. In the presence of iodide, the sensitivity is of the order of 2×10^{-5} concentration of iodine. Heat decreases the sensitivity, as does alcohol.

INDICATORS FOR PRECIPITATION REACTIONS

In precipitation reactions, application of the differences in solubility is made. To take a concrete example,

¹⁰ M. Starr Nichols, *J. Ind. Eng. Chem., Anal. Ed.*, 1, 215 (1929).

the reason that potassium chromate can be used as an indicator in the standardization of silver nitrate with sodium chloride may be explained in the following manner: The solubility of silver chloride is extremely small and that of silver chromate relatively large, so that no silver chromate will be formed until all chloride ions have been precipitated. Ferric alum acts in a similar manner in the silver nitrate-ammonium thiocyanate reaction.

GENERAL DISCUSSION

The short list of indicators already described should in no way be taken as representative of indicators as a whole. They are discussed only from the standpoint of their usefulness in standardization of normal solutions. Some indicators such as thymol blue and 4-nitrocatechol¹¹ exhibit three color changes, representing two transition intervals, one in the acid range, and one in the alkaline. Often, two indicators are mixed^{12, 13, 14} to give a transition range between certain pH values.

New oxidation-reduction indicators are constantly being prepared and tested. It has been found that the

¹¹ S. R. Cooper and V. J. Tulane, *J. Ind. Eng. Chem., Anal. Ed.* **8**, 210 (1936).

¹² H. A. J. Pieters, *Chem. Weekblad* **32**, 539.

¹³ Kurt Hoppner, *Deut. Zuckerind.* **61**, 361 (1936).

¹⁴ Kolthoff and Furman, *Volumetric Analysis, Vol. II* (1929), p. 64.

sodium or barium salt of diphenylamine sulphonic acid¹⁵ is a suitable oxidation-reduction indicator, particularly in presence of tungstates. In this respect, it is better than either diphenylamine or diphenylbenzidine, since tungstates interfere with these indicators.

Phenylanthranilic acid,^{16, 17} para and meta tolylphenylamine, and naphthidine¹⁸ have been proposed and used.

There is little to be said regarding adsorption indicators, as they are seldom used in procedures for standardizations. Fluorescein and eosin have been known and used for some time in the determination of halogens as the silver halides. Sodium rhodizonate^{19, 20} (sodium salt of tetrahydroxy quinone) is being used as an internal indicator for the determination of sulphates volumetrically. In the use of these indicators, there is a tendency toward an indicator lag, particularly in solutions of fairly high concentrations.

¹⁵ L. A. Sarver and I. M. Ko'thoff, *J. Am. Chem. Soc.* **53**, 2902, 2906 (1931).

¹⁶ A. U. Kirsanov and U. M. Cherkasou, *Zavodskaya Lab.* **5**, 143; *Bull. Soc. Chim. (5)*, **3**, 817.

¹⁷ V. S. Svirokomskii and V. V. Stepin, *J. Am. Chem. Soc.* **58**, 928 (1936).

¹⁸ Leora E. Straka with R. E. Oesper, *J. Ind. Eng. Chem., Anal. Ed.* **6**, 465 (1934).

¹⁹ Mutschin and Pollak, *Z. Anal. Chem.* **108**, 8 (1937).

²⁰ Mutschin and Pollak, *Z. Anal. Chem.* **108**, 309 (1937).

SUPPLEMENTARY REFERENCES

A Symposium on Indicators, *Chemical Reviews* 16, 53 (1935).

Advances in Indicators for Use in Volumetric Analysis, A. E. Jennings, Jr., *Can. Chem. Met.* 20, 220 (1935).

Chromotropic Acid as an Indicator in Fluorescence—Volumetric Analysis, Kocsis and Nagy, *Z. Anal. Chem.* 108, 317 (1937).

Indicators, I. M. Kolthoff, *J. Ind. Eng. Chem., Anal. Ed.* 8, 237 (1936).

Diphenylcarbazide, An Internal Indicator for Use in the Titration of Iron with Dichromate, H. E. Crossley, *Analyst*, 61, 164.

Internal Indicator for Dichromate-Titration of Iron, M. E. Weeks, *J. Ind. Eng. Chem., Anal. Ed.* 4, 127 (1932).

Oxidation-Reduction Indicators for Use with Dichromate II, Stuart Cohen and Ralph E. Oesper, *J. Ind. Eng. Chem., Anal. Ed.* 8, 364 (1936).

A Better Titrating Solution Using Diphenylamine Indicator, W. K. Gibson, *Chemist-Analyst* 26, 28 (1937).

Indicator: Ferrous-ortho-phenanthroline, Walden, Hammet, and Chapman, *J. Am. Chem. Soc.* 53, 3908 (1931).

Starch Indicator, Fales, *Inorganic Quantitative Analysis* (The Century Co., New York, 1925), 300.

The Constitution of Starch Iodide, A. Lottermoser, *Z. Angew. Chem.* 34, Aufsatzteil, 427 (1921); *Chemical Abstracts* 16, 10 (1922).

The Taking Up of Iodine by Various Substances, A. Lottermoser, *Kolloid Z.* 33, 271 (1923); *Chemical Abstracts* 18, 925 (1924).

Starch Iodide, A. Lottermoser, *Z. Angew. Chem.* 37, 84 (1924); *Chemical Abstracts* 18, 950 (1924).

CHAPTER IV

Standard Substances

IF THE concentration of a solution is to be determined accurately, it is necessary to compare it with some substance of known purity. Not all substances are suitable for standards, and, because of this fact, certain requirements are necessary, chief among which are high equivalent weight, stability at ordinary temperatures, ease of purification, solubility and absence of side reactions. The substance should neither deliquesce nor effloresce.

Many attempts have been made to prepare a universal primary standard, but, so far, such work has not been successful. There are, however, many excellent primary standards available. Some of these overlap, that is to say, they may be used as a standard for more than one type of standard reaction. They may be placed in general classifications as follows:

1. Standard substances for acids and bases
2. Standard substances for precipitation reagents
3. Standard substances for oxidation-reduction reagents

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Considering the first class of standards, they may be further subdivided into those suitable for acids and those suitable for bases. In the first category falls anhydrous sodium carbonate, the classical primary standard for acids. In spite of the recognized shortcomings, it has stood the test of time. Extreme care, however, must be exercised in using it, both in preparation and in standardization. Smith and Croad¹ have found that it is not safe to heat the bicarbonate above 300° C in preparing the carbonate, as there is appreciable decomposition at 310–315° C. Sodium carbonate suitable for standardization purposes, according to Stalony-Dobrzanski,² is obtained by heating sodium bicarbonate between 150 and 280° C. Decomposition of the sodium bicarbonate is completed after 100 minutes. There is also a disadvantage of low equivalent weight and the fact that it is hygroscopic.

Borax, originally used in the anhydrous state, was unsatisfactory due to the difficulty in preparing and keeping the anhydrous salt. The decahydrate,^{3, 4, 5} how-

¹ G. F. Smith and G. F. Croad, *Ind. Eng. Chem., Anal. Ed.* **9**, 141 (1937).

² J. Stalony-Dobrzanski, *Roczniki Chem.* **14**, 1106 (1934).

³ G. Kilde, *Dansk. Tids. Farm.* **10**, 273 (1936), (English summary).

⁴ F. H. Hurley, Jr., *Ind. Eng. Chem., Anal. Ed.* **8**, 220 (1936).

⁵ F. H. Hurley, Jr., *Ind. Eng. Chem., Anal. Ed.* **9**, 237 (1937).

ever, makes a suitable standard which possesses the advantage of a high equivalent weight.

Carlton⁶ proposed the use of symmetrical diphenyl guanidine, but a comparison made by Thornton and Christ⁷ showed that the results obtained were low and suggested that a better method of purification was necessary if it was to be used as a standard. On the other hand, Young⁸ states that it may be purified simply by recrystallization to provide a satisfactory primary standard. Guanidine carbonate,⁹ prepared from calcium cyanide, is very pure, contains no water of crystallization, and is not hygroscopic. It behaves as a monoacidic base and is accurate enough for use as a standard in routine work.

Potassium bicarbonate,^{10, 11, 12, 13} as an acidimetric standard, is prepared by passing CO₂ into an alcoholic solution of potassium hydroxide. It is a reliable standard for all but very accurate work. Solutions stronger than N/10 show a tendency to evolve CO₂.

⁶ C. A. Carlton, *J. Am. Chem. Soc.* **44**, 1469 (1922).

⁷ W. M. Thornton and C. L. Christ, *Ind. Eng. Chem., Anal. Ed.* **9**, 339 (1937).

⁸ J. W. Young, *Can. J. Research* **17B**, 192 (1939).

⁹ A. H. Dodd, *J. Soc. Chem. Ind.* **40**, 80-90 T (1921).

¹⁰ L. W. Winkler, *Z. angew. Chem.* **28**, 264 (1915); *Chemical Abstracts* **9**, 2747 (1915).

¹¹ G. Incze, *Z. anal. Chem.* **54**, 585 (1916).

¹² G. Bruhns, *Chem. Ztg.* **41**, 386 (1917); *J. Chem. Soc.* **112**, II, 419.

¹³ G. Bruhns, *Chem. Ztg.* **48**, 89 (1924).

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Dipotassium periodate,¹⁴ $K_2H_3IO_6 \cdot 3H_2O$, reacts quantitatively with strong acids in the following manner:



It has the advantage of a relatively high equivalent weight. A sharp end point is obtained with methyl red as an indicator.

The use of thallous carbonate has been suggested by Hac and Kamen.¹⁵ As a result of their experiments, they concluded that it was a satisfactory primary standard. Reproducible results, using methyl orange as an indicator, were obtained, which agreed within a few thousandths of 1%, and the values compared favorably to those resulting from the use of Na_2CO_3 , $Na_2B_4O_7$ and $Na_2C_2O_4$. Work by Berry,¹⁶ and Jensen and Nilsen¹⁷ gives further proof of the suitability of thallous carbonate.

A method of great precision for the standardization of hydrochloric acid is the use of metallic silver¹⁸ as

¹⁴ L. Malaprade, *Congr. chim. ind., Compt. rend. 18 ème Congr. Nancy Sept.-Oct. (1938)*, 91.

¹⁵ R. Hac and K. Kamen, *Collection Czechoslov. Chem. Commun.* 4, 145; *Chem. Listy* 26, 6 (1932); *Chemical Abstracts* 26, 3746 (1932).

¹⁶ A. J. Berry, *Analyst*, 64, 27 (1939).

¹⁷ Einar Jensen and Bailli Nilssen, *Ind. Eng. Chem., Anal. Ed.* 11, 508 (1939).

¹⁸ C. W. Foulk and L. A. Pappenhaben, *Ind. Eng. Chem., Anal. Ed.* 6, 430 (1934).

an ultimate standard. It is a useful nephelometric method, and the results obtained exceed those of other methods in accuracy.

Another substance obtainable in a high degree of purity is yellow mercuric oxide.^{19,20} It is not hygroscopic and contains no water of crystallization. The principle depends upon the following reaction:



The mercuric oxide is dissolved in a large excess of potassium iodide (0.5 gm HgO and 7.5 gm KI), and the resulting potassium hydroxide is titrated with the acid to be standardized, using phenolphthalein as an indicator. Kolthoff and van Berk²¹ observe that whereas results by this method are accurate to within 0.1%, the method is not as precise as standardization with borax. Lazarkevich²² confirms this and states that mercuric oxide should be used only for rough work.

A report by Vandaveer²³ on the standardization of acidimetric solutions compares the results obtained by

¹⁹ L. Rosenthaler and A. Abelmann, *Pharm. J.* 91, 144, 186; *Chemical Abstracts* 7, 3726 (1913).

²⁰ G. Incze, *Z. anal. Chem.* 56, 177 (1917); *J. Soc. Chem. Ind.* 36, 671 (1917).

²¹ I. M. Kolthoff and L. H. van Berk, *Z. anal. Chem.* 71, 339 (1927).

²² N. A. Lazarkevich, *Ukrainskii Khem. Zhur.* 4, Sci. Pt. 405 (1929); *Chemical Abstracts* 24, 3456 (1930).

²³ R. L. Vandaveer, *J. Assoc. Official Agri. Chem.* 22, 563 (1939).



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standardizing 0.1*N* HCl with borax, sodium carbonate, and by precipitation as silver chloride. Considerable merit is claimed for borax and carbonate, but the results by silver chloride precipitation are not satisfactory, due, primarily, to the solubility of silver chloride.

Bromocyanogen²⁴ has been proposed as a universal standard for acids, silver nitrate, and sodium thiosulphate. It is, however, a disagreeable compound to work with, and its use is limited.

The standardization of bases by titration with a previously standardized acid is suitable for control work, but is affected, naturally, by those errors occurring in the initial standardization. It is necessary, therefore, to apply the same procedure to bases as was used for acids, namely, titration by means of a primary standard.

An early attempt to establish a universal standard was the use of ammonium triiodate, $(\text{NH}_4)_2\text{H}_2(\text{IO}_3)_3$.²⁵ It was prepared by the action of ammonium chloride on iodic acid, allowing the solution to stand 24-48 hours, and recrystallizing the salt from hot water. It contains no water of crystallization and can be dried over sulphuric acid. Borax²⁶ may be used for strong bases. Boric acid is very weak and can be titrated only in fairly high concentrations using a reference solution. It does, however, form compounds with polyhydric alco-

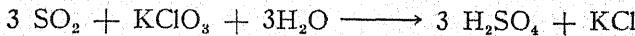
²⁴ M. Moller, *Z. anal. Chem.* 99, 351 (1934).

²⁵ E. Riegler, *Bull. assoc. chim. sucr. dist.* 24, 528; *Chemical Abstracts* 1, 705 (1907).

²⁶ M. G. Mellon and V. N. Morris, *Ind. Eng. Chem.* 17, 145 (1925).

hols, giving strong complex acids which give a sharp end point with phenolphthalein. Glycerine (neutral), glucose, or mannitol may be used. Mannitol is very satisfactory, but when glycerine is used, there is an indicator lag.

The use of potassium chlorate as a standard for alkali has been suggested by van Valkenburg.²⁷ A solution of the salt (approximately normal) is boiled and reduced, while boiling, with SO_2 according to the equation:



The excess SO_2 is boiled off, and the acid titrated with alkali, using phenolphthalein as an indicator.

Potassium binoxalate,²⁸ and either potassium or sodium acid phthalate²⁹ are suitable standards, the phthalates, in particular, because of their high equivalent weights.

Ashley and Hulett³⁰ proposed the use of cadmium sulphate as a standard for alkali. They allowed a solution of the salt to evaporate spontaneously and separated the clear crystals. From a given weight of the clear crystals, a known quantity of sulphuric acid

²⁷ H. B. van Valkenburg, *J. Am. Chem. Soc.* **42**, 757 (1920).

²⁸ Yukichi Osaka and Kinji Ando, *J. Tokyo Chem. Soc.* **41**, 945 (1920); *Chemical Abstracts* **15**, 1472 (1920).

²⁹ W. S. Hendrixson, *J. Am. Chem. Soc.* **37**, 2352 (1915).

³⁰ S. E. Q. Ashley and G. A. Hulett, *J. Am. Chem. Soc.* **56**, 1275 (1934).

was obtained by dissolving the sulphate in water and depositing the cadmium on a mercury cathode. The results agreed with values obtained using benzoic acid, potassium acid phthalate, and constant-boiling hydrochloric acid.

By far the largest class of compounds available for the standardization of bases is the organic acids. Their solubility in water is usually low and they are, for the most part, dissolved and titrated in an alcohol-water mixture.

Phelps and Weed³¹ examined a number of organic compounds, namely, succinic acid, succinic anhydride, malonic acid, benzoic acid, phthalic acid, and phthalic anhydride and found excellent agreement. On the other hand, Peters and Sanchelli³² were unable to duplicate the work of Phelps and Hubbard³³ who had previously used succinic acid for standardizing ammonia. These authors obtained normalities which were high compared with those measured by other methods. Correct results, according to Ljungren,³⁴ may be obtained with *N*/10 alkalies by dissolving succinic acid in a

³¹ I. K. Phelps and L. H. Weed, *Am. J. Sci.* **26**, 138 (August).

³² C. A. Peters and V. Sanchelli, *Am. J. Sci.* **41**, 244 (1916).

³³ I. K. Phelps and J. L. Hubbard, *Am. J. Sci.* **23**, 211; *Z. anorg. Chem.* **53**, 361; *Chemical Abstracts* **1**, 1832 (1907).

³⁴ G. Ljungren, *Svensk Kem. Tid.* **36**, 25 (1923); *Chemical Abstracts* **18**, 1447 (1924).

minimum quantity of CO_2 -free water (no more than 10 cc), and using 3-4 drops of 1:1000 phenolphthalein solution as an indicator.

Adipic acid^{35, 36} and salicylic acid³⁷ are satisfactory standards, although the values obtained with the latter³⁸ are somewhat low. Furoic acid,³⁹ which possesses the advantage of being soluble in water, gives about the same accuracy as benzoic acid. Aminosulphonic acid⁴⁰ and the sulphuric acid salts of aromatic amines⁴¹ have also been used and are capable of reasonable accuracy.

Sulphamic acid, $\text{NH}_2\text{SO}_3\text{H}$,⁴² has been proposed as an alkalimetric standard. It is easily purified, is not hygroscopic, and is soluble in water. Aqueous solutions hydrolyze, on standing, to ammonium acid sulphate.

The standardization of silver nitrate solutions is accomplished either gravimetrically or volumetrically; the

³⁵ F. Th. van Voorst, *Chem. Weekblad*, **25**, 22 (1928).

³⁶ A. H. Meyling, *J. S. African Chem. Inst.* **18**, 23 (1935).

³⁷ J. Rosicky and J. Tamchyna, *Chem. Listy*, **25**, 468 (1931); *Chemical Abstracts* **26**, 4006 (1932).

³⁸ S. Skromovsky, *Collection Czechoslov. Chem. Communications* **5**, 143 (1933); *Chemical Abstracts* **27**, 3418 (1933).

³⁹ H. B. Kellogg and Ada M. Kellogg, *Ind. Eng. Chem., Anal. Ed.* **6**, 251 (1934).

⁴⁰ L. Herboth, *Arch. Phar.* **262**, 517 (1924).

⁴¹ E. Strasser, *Z. anal. Chem.* **82**, 114 (1930).

⁴² Sister M. Josetta Butler, G. F. Smith and L. F. Andrieth, *Ind. Eng. Chem., Anal. Ed.* **10**, 690 (1938).

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former by precipitation of the silver as silver chloride with a slight excess of sodium chloride to which a small amount of nitric acid has been added, and the latter by titration of known amounts of pure sodium chloride with potassium chromate as an indicator. A blank determination, using the same amount of indicator as in the sample, must be run and the correction subtracted from the sample titration. Ammonium thiocyanate and potassium thiocyanate are generally standardized by direct titration with standard silver nitrate solution, although the recrystallized salt may be used.

The evaluation of potassium ferrocyanide solutions is made with pure zinc oxide. This can be purchased in a high degree of purity and, after a preliminary drying for an hour at 105° C, is ready for use.

On account of its stability and the ease with which it is purified, potassium dichromate still remains an excellent standard substance for sodium thiosulphate solutions. Conflicting statements, however, have appeared in the literature concerning its use in the procedure. Vosburgh⁴³ states that if the solution is 0.2–0.4 N in HCl, contains 2–3 gm of potassium iodide for every five milliequivalents of dichromate, and is allowed to stand in the dark for 4–10 minutes, the reduction is quantitative. The solution is then diluted to 400 cc with distilled water, and titrated with the thiosulphate solution.

⁴³ W. C. Vosburgh, *J. Am. Chem. Soc.* 44, 2120 (1922).

On the other hand, Jander and Berte⁴⁴ add 15 cc of $N/10$ $K_2Cr_2O_7$ to 40 cc of 2 N KI and 40 cc of concentrated HCl. Complete liberation of iodine takes place in fifteen minutes. If the solution is titrated too quickly, too much thiosulphate is used. Their values, using this procedure, agreed exactly with those obtained by standardization of thiosulphate solution with potassium permanganate and pure iodine.

The reliability of the results, obtained by the use of this standard, has often been questioned. It has been suggested⁴⁵ that variations occur due to air oxidation of potassium iodide, and that the reaction is catalyzed by Cr^{+++} ions. Teis⁴⁶ found that variable results were obtained when the concentration of potassium iodide, and the time of standing were varied.

Potassium iodate and potassium bromate are satisfactory standards for thiosulphate solutions, but unsatisfactory from the standpoint of their low equivalent weights. Milstead,⁴⁷ however, reporting on the standardization of iodine and thiosulphate solutions, states that normalities obtained by use of iodine and unpuri-

⁴⁴ G. Jander and H. Berte, *Z. anorg. allgem. Chem.* 113, 73 (1924).

⁴⁵ K. Bottger and W. Bottger, *Z. anal. Chem.* 69, 146 (1926).

⁴⁶ R. V. Teis, *J. Gen. Chem. (U.S.S.R.)* 1, 845 (1931); *Chemical Abstracts* 27, 39 (1933).

⁴⁷ K. L. Milstead, *J. Assoc. Official Agri. Chem.* 22, 567 (1939).

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fied analytical grade potassium iodate do not agree, and that some impurity was present which liberated more iodine than a corresponding amount of iodate. The amount of this impurity, which was thought to be sodium iodate, appeared greater after recrystallization.

The use of potassium iodide in the standardization of solutions of low normality has been suggested by Hurka.⁴⁸ Briefly, the iodide is oxidized by bromine to iodate, which, in turn, is reacted with sulphuric acid, liberating iodine, which is titrated with the thiosulphate.

Potassium permanganate⁴⁹ has been used as a standard for sodium thiosulphate, and accurate results were obtained, providing that the conditions were strictly adhered to. The reaction between $KMnO_4$ and KI takes place in 50–125 cc of 0.7–0.1 *N* HCl or H_2SO_4 . After standing 2–5 minutes, the solution is diluted to 600 cc and titrated.

Potassium biiodate,⁵⁰ oxalic acid,⁵¹ and copper^{52, 53}

⁴⁸ W. Hurka, *Mikrochemie ver. Microchim. Acta* **28**, 294 (1940).

⁴⁹ J. M. Hendel, *Z. anal. Chem.* **63**, 321 (1923).

⁵⁰ M. Koenig, *Chimie et industrie*, Special No. 116–7 (Sept. 1925).

⁵¹ N. A. Tananaev and N. A. Lazarkevich, *J. Russ. Phys. Chem. Soc.* **61**, 1909 (1929); *Chemical Abstracts* **24**, 3456 (1930).

⁵² T. F. Buerer and C. M. Mason, *Ind. Eng. Chem., Anal. Ed.* **1**, 68 (1929).

⁵³ S. Popoff, Margaret Jones, C. Rucker and W. W. Becker, *J. Am. Chem. Soc.* **51**, 1299 (1929).

have been suggested as standard substances for thiosulphate solutions. Potassium biiodate can be obtained in a high state of purity, but possesses a low equivalent weight. The titration is carried out in a solution slightly acid with HCl.

If sodium thiosulphate is decomposed by HCl and converted to Na_2CO_3 by ignition with oxalic acid, the Na_2CO_3 may be titrated with standard acid, and the thiosulphate solution evaluated in this manner.

The use of copper * as an analytical standard must depend on the purity of the sample. Copper produced electrolytically is the best source. It is dissolved in sulphuric acid, evaporated to dryness, and taken up in distilled water. The reaction proceeds in a neutral, or nearly neutral, solution in the absence of salts. Potassium iodide is then added to reduce the copper. Acid concentration affects the determination by lessening the amount of iodine liberated, and should not be over 0.2 N in sulphuric acid.

Several standard substances are available for the evaluation of iodine solutions. A method commonly used is the titration of the unknown solution with previously standardized sodium thiosulphate. This is necessarily open to errors, which may be additive, arising from the standardization of the thiosulphate solution.

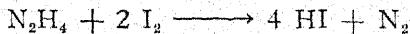
* See also, Copper Sulphate as a Standard for Thiosulphate Titrations, a review with discussion of the literature, N. Schoorl, *Pharm. Weekblad* 76, 1441 (1939).

Sodium thiosulphate pentahydrate is suitable as a standard substance. According to Kolthoff,⁵⁴ its range of stability is great. Below 23% relative humidity it weathers, and above 69% it deliquesces. The anhydrous salt is not recommended, as it is strongly hygroscopic.

Arsenious acid is a very satisfactory standard. It is stable and easily obtainable pure.

Sodium acetomercurithymol sulphonate⁵⁵ may be obtained in a high degree of purity. It has a high molecular weight, and reacts with iodine by displacement of the acetomeric group. It is stated to give more accurate results than arsenious oxide.

Hydrazine reacts with iodine according to the following equation :



It is used in the form of hydrazine sulphate, and the reaction takes place in a solution alkaline with sodium bicarbonate. A disadvantage is its low equivalent weight.

Ammonium triiodate,⁵⁶ silver nitrate,⁵⁷ and potassium

⁵⁴ I. M. Kolthoff and N. H. Furman, *Volumetric Analysis*, Vol. II (1929), p. 360.

⁵⁵ C. V. Bordeianu, I. N. Petrescu, L. Staicovici, *Bull. Soc. Stiinte Farm. Romania* 4, 473 (1939); *Chimie et industrie* 43, 458.

⁵⁶ E. Riegler, *Bull. assoc. chim. sucr. dist.* 24, 528; *Chemical Abstracts* 1, 705 (1907).

⁵⁷ V. E. Pavloc and S. D. Shein, *J. Russ. Phys. Chem. Soc.* 39, 943; *Chemical Abstracts* 2, 772 (1908).

stannous diaquotetrachloride ($K_2SnCl_4 \cdot 2 H_2O$)⁵⁸ have also been proposed as iodometric standards.

The usual method of standardization of potassium permanganate is by means of oxalic acid or sodium oxalate. Hill and Smith⁵⁹ recrystallized oxalic acid ($H_2C_2O_4 \cdot 2 H_2O$), and found that values obtained with permanganate agreed within 0.025% with those obtained using Bureau of Standards sodium oxalate. The vapor pressure of the hydrate at ordinary temperatures is slightly less than that of air at the same temperature. There is, therefore, danger of water condensing as a film on the surface of the crystals. Treadwell and Johner⁶⁰ recommend drying the recrystallized and powdered acid in a stream of air which has been passed through a mixture of equal parts of hydrated and hydrous acid. The results, using this procedure, are comparable to those obtained by use of sodium oxalate. Calcium oxalate,⁶¹ prepared from pure calcium oxide, has been used as a standard substance, and satisfactory results are claimed for it.

The use of metallic silver⁶² has been proposed, and

⁵⁸ T. Karantarsis and L. Capatos, *Compt. rend.* **194**, 1839 (1932).

⁵⁹ A. E. Hill and T. M. Smith, *J. Am. Chem. Soc.* **44**, 546 (1922).

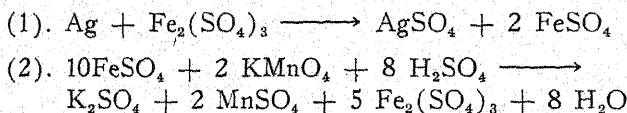
⁶⁰ W. D. Treadwell and H. Johner, *Helv. Chim. Acta* **7**, 528 (1924).

⁶¹ E. Little and W. H. Beisler, *J. Am. Leather Chem. Assoc.* **14**, 613 (1919).

⁶² N. A. Tananaev, *Z. anorg. allgem. Chem.* **136**, 193 (1924).

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the standardization of permanganate by it is obtained in the following manner: Ferric alum (0.5–1.0 gm) is dissolved in 100 cc of 7 *N* H₂SO₄ in an Erlenmeyer flask. The solution is saturated with CO₂, and 0.25–0.35 gm silver added. After the silver has dissolved, the solution is cooled rapidly, phosphoric acid added until the solution is colorless, and titrated with permanganate. The reactions involved take place as follows:



The use of iron, Mohr's salt, and arsenious oxide is not entirely satisfactory, since they all possess disadvantages. The purity of iron and Mohr's salt is questionable, and if it is necessary to establish the purity of these compounds by some other means, they lose their significance as standard substances. Ferric ammonium sulphate, which can be obtained pure by recrystallization, may be used as a standard, first reducing all the ferric iron to ferrous iron. Its keeping qualities are not good. The reaction with arsenious oxide does not proceed smoothly. Complex compounds are formed, and the end point is not well defined. Potassium ferrocyanide has been used as a standard substance, but the end point, which is difficult to detect, offsets the advantage of a high equivalent weight. Titration must take

place in dilute solution. DeBeer and Kjort⁶³ have used ferrocyanide for the standardization of dilute solutions, with erioglaucine as an indicator.

Evidence has been presented⁶⁴ to show that results of standardization of permanganate with sodium oxalate are not reliable to less than 1 part in 1000. Fused potassium iodide, titrated by Andrew's method to ICl , shows agreement within 0.03%, and may be regarded as a more reliable standard.

Further work⁶⁵ with potassium iodide for standardization of strong oxidizing agents such as permanganate and ceric sulphate involves the use of acetone. The iodide is dissolved in water acid with H_2SO_4 , and pure acetone added. The solution is titrated with the oxidizing agent, using three drops of 0.025 *N* ferrous phenanthroline sulphate as an indicator. The end point is reached when the solution remains colorless for thirty seconds. The results are generally low, due to a reaction between acetone and the oxidizing agent.

⁶³ E. J. deBeer and A. M. Hjort, *Ind. Eng. Chem., Anal. Ed.* 7, 120 (1935).

⁶⁴ I. M. Kolthoff, H. A. Laitinen and J. J. Lingane, *J. Am. Chem. Soc.* 59, 429 (1937).

⁶⁵ I. M. Kolthoff and H. A. Laitinen, *J. Am. Chem. Soc.* 61, 1690 (1939).

CHAPTER V

Standard Solutions of Acids and Bases

STANDARDIZATION OF HYDROCHLORIC ACID

Molecular Weight:	36.465	HCl
Equivalent Weight:	36.465	
Grams of Constant Boiling Acid/Liter for		
1	Normal Acid 180.193 gm	
0.5	" " 90.097 gm	
0.1	" " 18.019 gm	

Preparation of Constant Boiling Acid

Since ordinary concentrated hydrochloric acid¹ varies slightly in strength, it would seem useful to have some definite standard solution which would not vary in percentage composition. Hulett and Bonner² recommended the use of constant-boiling acid for standard solutions. Foulk and Hollingsworth³ made an extremely accurate investigation. They recommend start-

¹ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

² G. A. Hulett and W. D. Bonner, *J. Am. Chem. Soc.* 31, 390 (1909).

³ C. W. Foulk and M. Hollingsworth, *J. Am. Chem. Soc.* 45, 1220 (1923).

ing with hydrochloric acid solution of specific gravity 1.18. After three-quarters of the mixture have been distilled, the receivers are changed and the distillation continued until only a few cubic centimeters are left in the still. This last distillate is considered to be constant-boiling acid. The speed of distillation has very little influence on the acid content. If, however, the original acid is diluted to a specific gravity of 1.0959 at 25° C, three-quarters of the distillate may be used. Discard the first quarter and continue distillation until only 50–60 cc are left. In this way, it is easy to obtain a definite standard solution within an accuracy of 0.05 per cent.⁴ Barometric pressure must be recorded, as the percentage composition varies. The following table (after Foulk and Hollingsworth)³ gives the composition of constant-boiling acid at various pressures.

Pressure during Distillation mm of Mercury	% HCl Referred to Vacuum	Wt. of Distillate Containing 1 Mol of HCl when Weighed on Air
780	20.173	180.621
770	20.197	180.407
760	20.221	180.193
750	20.245	179.979
740	20.269	179.766
730	20.293	179.551

Store the constant-boiling acid in glass-stoppered bottles. From the barometric pressure, calculate the percentage composition and label the bottles accordingly.

⁴ Kolthoff and Furman, *Volumetric Analysis Vol. II*, 74 (1929).

*Standardization of Normal and Half Normal Acid
with Sodium Carbonate*

If the distillation of constant-boiling acid has been carried out at 760 mm, weigh out accurately 180.193 gm and 90.097 gm respectively for normal and half normal acid and make up to 1 liter with distilled water; otherwise weigh accurately equivalent amounts depending on the barometric pressure at the time of distillation.

According to Lunge, sodium bicarbonate is quantitatively converted into the carbonate by heating to 270–300° C. The procedure is as follows: Place 10 gm of the bicarbonate⁵ in a silver crucible, and place in a shallow sand bath, imbedding the crucible so that the level of the sand is slightly above the level of bicarbonate in the crucible. Suspend a thermometer in the crucible in such a way that it acts as a stirring rod. Heat the sand bath so that the temperature rises at the rate of 5° C a minute, stirring the bicarbonate continually. This stirring is important, especially when relatively large amounts are to be converted to carbonate. After heating between 270 and 300° C for at least half an hour, the crucible is transferred to a desiccator and cooled. A recent paper by Smith and Croad⁶

⁵ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* **18**, 759 (1926).

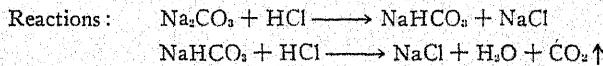
⁶ G. F. Smith and G. F. Croad, *J. Ind. Eng. Chem., Anal. Ed.* **9**, 141 (1937).

has shown that an appreciable error results when the temperature is allowed to exceed 300° C. The carbonate is transferred to a bottle having a tight-fitting, ground glass stopper. When weighing, the bottle should be opened only for brief intervals, and the weighing accomplished as quickly as possible, because of the fact that carbonate changes to the monohydrate rapidly.

If, for any reason, it is inconvenient to prepare carbonate from the bicarbonate, it is possible to use an analytical grade sodium carbonate, after washing with alcohol and drying at 100° C, since the chief impurity is sodium hydroxide, which is soluble in alcohol.

Procedure for Standardization

Weigh out sufficient sodium carbonate to give a titration of around 40 cc. In the case of normal acid, use 2.12 gm, and 1.06 gm for half normal acid. Dissolve the carbonate in the smallest possible quantity of water. Titrate, using methyl yellow as an indicator, to the first change. Just before the end point is reached, the solution should be stirred or shaken vigorously to remove carbon dioxide.

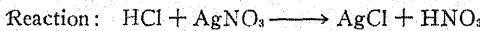


Calculations : Equivalent weight of $\text{Na}_2\text{CO}_3 = 53.0$

$$\text{Normality} = \frac{\text{Weight of } \text{Na}_2\text{CO}_3}{0.053 \times \text{Titration in cc}}$$

Standardisation of Tenth Normal Acid by Precipitation as Silver Chloride

Tenth normal acid is prepared by accurately pipetting 100 cc of normal acid into a volumetric flask and diluting to one liter. It is standardized as follows: Pipette 50 cc portions into 250 cc beakers. Add an excess of silver nitrate solution to precipitate the acid as silver chloride. Bring to a boil to coagulate the precipitate. Let stand in the dark until cool, and filter through previously dried and weighed Gooch crucibles.



Mol wt. AgCl = 143.34 1 cc HCl ≈ 0.14334

Wt. of silver chloride

$$\text{Calculations: Normality} = \frac{\text{Wt. of silver chloride}}{50 \times 0.14334}$$

Alternative Method of Standardization Using Borax

Borax⁷ has long been recognized as a primary standard for acids. The greatest obstacle, however, has been the difficulty in preparing the anhydrous salt and preserving it in the anhydrous state. In an article,^{8, 10} it is stated that borax, recrystallized as the decahydrate from water and kept over a solution of sodium bromide having a relative humidity of 60%, is extremely stable over a long period. Added to this is the advantage that borax does not lose water of crystallization during the time of weighing.

⁷ Kolthoff and Furman, *Volumetric Analysis Vol. II*, 93 (1929).

Pure borax may be prepared as follows⁸: 45 gm of borax are added to 150 cc of water at room temperature, stirred well, and allowed to stand for several hours. The borax is filtered off through a Büchner funnel, washed twice with water, then with two portions of 95% ethyl alcohol, and finally twice with ethyl ether, each washing being followed by suction to remove the wash liquid. Use 5 cc of alcohol and ether for every 10 gm of borax. Transfer the crystals to a watch glass, and allow them to stand at room temperature a short time to permit evaporation of the ether, then transfer them to a desiccator containing a saturated sodium chloride solution as a desiccant. It was found that sodium chloride could be substituted for sodium bromide, since the relative humidity of the saturated solution⁹ is 60%. To insure the crystals reaching equilibrium, they should be left in the desiccator for a week before using.

Standardization of Normal, Half Normal, and Tenth Normal Acid

Prepare the normal solutions in accordance with the instructions given in the preceding methods.

Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$, has a molecular weight of 381.43, and an equivalent weight of 190.76, which

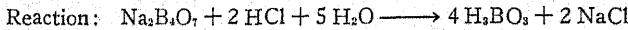
⁸ F. H. Hurley, *J. Ind. Eng. Chem., Anal. Ed.* 8, 220 (1936).

⁹ Kolthoff and Sandell, *Inorg. Quant. Analysis* (1929), 123.

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means that large samples can be used for standardization, thus reducing the error in weighing.

The procedure is as follows: Weigh out 6.00 gm, 3.00 gm, and 0.65 gm respectively for normal, half normal, and tenth normal acid. Dissolve in the smallest quantity of distilled water. Add several drops of methyl red and titrate to the first visible change.



$$\text{Calculations: Normality} = \frac{\text{Wt. of Borax}}{0.19076 \times \text{Titration in cc}}$$

Note: In the standardization of tenth normal acid, it is necessary to boil the water first to remove carbon dioxide, since failure to do so introduces a real error in the standardization. In the case of normal and half normal acid, this precaution is not necessary.

Standardization of Normal, Half Normal, and Tenth Normal Acid with Thallous Carbonate

Thallous carbonate, with its high equivalent weight (468.79), is an excellent primary standard for acids and has also been used for the standardization of iodate solutions.

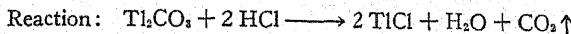
The following procedure for the standardization of acids is based on the method recommended by Berry.¹¹

A suitable quantity of the salt (or a corresponding volume of solution) is dissolved in distilled water and

¹⁰ F. H. Hurley, *J. Ind. Eng. Chem., Anal. Ed.* 9, 237 (1937).

¹¹ A. J. Berry, *Analyst*, 64, 27 (1939).

titrated, using methyl orange as an indicator.* The *pH* at the end point is 3.8.



$$\text{Calculations: Normality} = \frac{\text{Wt. Ti}_2\text{CO}_3}{0.46879 \times \text{cc Titration}}$$

STANDARDIZATION OF SULPHURIC ACID

Molecular Weight: 98.08 H_2SO_4

Equivalent Weight: 49.04

Preparation of the Solution

Weigh accurately the amount of acid¹² necessary to give the required normality, taking into consideration the strength of the acid as recorded on the original container. Add cautiously to a relatively large amount of water, and when cool, transfer to a volumetric flask and make up to volume.

Standardization with Barium Chloride

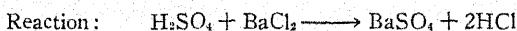
Pipette 25 cc of the volumetric solution into a 400 cc beaker, add 250 cc of distilled water and 3 cc of concentrated hydrochloric acid. Heat to boiling and precipitate at the boil with 10% barium chloride. Allow

*Hickman and Linstead [*J. Chem. Soc.* 121, 2502 (1922)] recommend screening the methyl orange indicator with xylene cyanine FF.

¹² Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem., Anal. Ed.* 17, 756 (1925).

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the barium chloride¹² to run in drop by drop, stirring vigorously meanwhile. Popoff¹³ has shown that the temperature at which the barium sulphate is precipitated influences greatly the size of the crystals. Cover the beaker with a watch glass and let the precipitate stand over night on the steam plate. Filter, hot, through a quantitative filter paper, and wash the precipitate at least ten times with hot water, or until the filtrate gives no precipitate with silver nitrate. Ash carefully in a platinum crucible, or a clean porcelain crucible, to constant weight.



$$\text{Calculations: Factor } \frac{\text{H}_2\text{SO}_4}{\text{BaSO}_4} = \frac{98.08}{233.42} = 0.4202$$

$$0.4202 \times \frac{1000}{25} \times \text{wt. of ppt.} = \text{wt. of H}_2\text{SO}_4 \text{ in gm/l}$$

$$\text{Normality} = \frac{49.04}{\text{wt. of H}_2\text{SO}_4}$$

The standardization of sulphuric acid is accomplished most accurately by precipitation as barium sulphate. However, the methods involving the use of borax or carbonate, as described under hydrochloric acid, give equally accurate results.

Note: Picric acid (10 cc of a saturated solution) may be added to the sample of sulphuric acid to be standardized, before precipitation as barium sulphate. The solution is brought to boiling and the

¹² S. Popoff and E. W. Neuman, *Ind. Eng. Chem., Anal. Ed.* 2, 45 (1930).

usual procedure for precipitation followed. If the solution is boiled gently for 5-10 minutes, and then allowed to stand on a steam plate for an hour, the precipitate may be filtered, ignited, and weighed. The results obtained may not be strictly accurate, since, if the filtrate from this procedure is allowed to stand over night, it is possible to obtain a slight amount of precipitate, representing barium sulphate, which, at the time of filtration, was in the colloidal state. It is also important that the acidity, after precipitation, should not be too high, since hydrochloric acid exerts a solvent effect, or possibly a peptizing action on freshly precipitated barium sulphate. Picric acid may contain soluble sulphate as an impurity. If there is any doubt as to the purity, it is necessary to run a blank determination on the amount of picric acid ordinarily used in the determination.

STANDARDIZATION OF SODIUM HYDROXIDE

Preparation of the Solution

Standard solutions of sodium hydroxide ¹⁴ should be prepared from a concentrated stock solution.^{15, 16} This is a 50% solution, so called Sörenson's "oily alkali," and is made by dissolving one pound of pellet caustic in 450 cc of distilled water. The solution will be cloudy, due to carbonate ¹⁷ which is always present. Let the solution stand for several days or until the carbonate has settled out and the liquid is clear, before using. If

¹⁴ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

¹⁵ Hillebrand and Lunden, *Applied Inorganic Analysis* (1929), 139.

¹⁶ Kolthoff and Furman, *Volumetric Analysis Vol. II* (1929), 77.

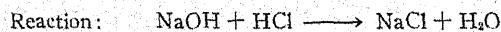
¹⁷ J. E. S. Han and T. Y. Chao, *J. Ind. Eng. Chem. Anal. Ed.* 4, 229 (1932).

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it is necessary to use immediately, the solution may be centrifuged.¹⁸ The solution is best kept in a Pyrex Erlenmeyer, tightly closed with a rubber stopper.

Standardization with Hydrochloric Acid

Weigh out the equivalent of alkali by withdrawing the stock solution by means of a pipette, and transferring to a weighing bottle. If tenth normal alkali, or less, is to be prepared, make up to volume with water which has been previously boiled to expel carbon dioxide. Pipette 25 cc of previously standardized hydrochloric acid into an Erlenmeyer flask and titrate to an end point, using phenolphthalein as an indicator. The accuracy of this standardization will depend upon the accuracy with which the normality of the hydrochloric acid was determined.



$$\text{Calculations: } N_{\text{NaOH}} \times V_{\text{NaOH}} = N_{\text{HCl}} \times V_{\text{HCl}}$$

where N = normality and V = volume of solution used

Standardization with Potassium Acid Phthalate^{19, 20}

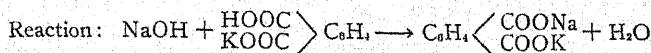
Potassium acid phthalate may be obtained pure from the Bureau of Standards, or the pure salt may be re-

¹⁸ N. Allen and G. W. Low, *J. Ind. Eng. Chem., Anal. Ed.* 5, 192 (1933).

¹⁹ F. E. Dodge, *J. Ind. Eng. Chem.*, 7, 29 (1915).

²⁰ W. S. Hendrixson, *J. Am. Chem. Soc.* 37, 2353 (1915); 42, 724 (1920).

crystallized from water and dried at 105° C. Weigh a sufficient quantity of the salt to give a titration of about 40 cc. Dissolve in a small quantity of distilled water and titrate with alkali to an end point with phenolphthalein.

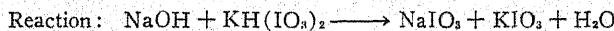


Calculations: The equivalent weight of potassium acid phthalate is 204.06

$$\text{Normality} = \frac{\text{Wt. of KHO}_4\text{C}_6\text{H}_4}{0.20406 \times \text{cc of alkali}}$$

Standardization with Potassium Bi-iodate

The salt may be obtained pure. If necessary, it can be recrystallized from water and dried at 105° C. It has the advantage of a high equivalent weight, and is not hygroscopic. Dissolve enough of the salt to give a titration of about 40 cc in a small quantity of distilled water and titrate using phenolphthalein as an indicator.



Calculations: The equivalent weight of potassium bi-iodate is 389.85

$$\text{Normality} = \frac{\text{Wt. of KH}(\text{IO}_3)_2}{0.3899 \times \text{cc of alkali}}$$

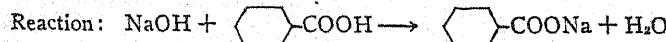
Standardization with Benzoic Acid

Pure benzoic acid may be purchased from the Bureau of Standards. It is, however, readily obtainable from other sources in a high degree of purity. Alcohol, which has been carefully neutralized to the phenolphthalein end point with alkali, is used as a solvent.



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A weighed quantity of benzoic acid, sufficient to give a titration of around 40 cc, is dissolved in 25 cc of the neutralized alcohol and titrated to an end point



Calculations: The equivalent weight of benzoic acid is 122.46

$$\text{Normality} = \frac{\text{Wt. of benzoic acid}}{0.1225 \times \text{cc of alkali}}$$

Standard solutions of alkali should be stored in bottles made of alkali-resistant glass. Ordinary glass bottles are appreciably attacked on standing. As a precaution against contamination of the standard alkali from carbon dioxide in the air, it is well to equip the containers with a soda-lime tube.

STANDARDIZATION OF POTASSIUM HYDROXIDE

Molecular Weight: 56.10
Equivalent Weight: 56.10

KOH

Preparation of the Solution

Potassium hydroxide,²¹ unfortunately, cannot be prepared carbonate-free as easily as sodium hydroxide, since potassium carbonate is appreciably soluble in the concentrated alkali. Kolthoff^{22, 23} suggests the follow-

²¹ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

²² I. M. Kolthoff, *Z. Anal. Chem.* 61, 48 (1922).

²³ Kolthoff and Furman, *Volumetric Analysis Vol. II* (1929), 77.

ing method: Prepare a 1.1 *N* solution of potassium hydroxide. Add 50-80 cc of milk of lime and shake for one hour. Allow to settle for several days and siphon off the clear liquid. The solution must be protected from the carbon dioxide of the air by means of a soda lime tube. After determining the normality of this stock solution, it may be diluted to the desired strength. If the directions are properly carried out, the solution will contain no more than 1-2 mg of calcium per liter. The presence of carbonate may be determined qualitatively by adding some of the alkali to a test tube containing *N*/2 barium nitrate or chloride, closing the tube quickly after addition, and shaking. No turbidity should form after ten minutes standing.

Carbonate-free potassium hydroxide may also be prepared by dissolving the alkali in a small quantity of alcohol. After the carbonate settles out, the clear solution is decanted into a volumetric flask containing previously boiled distilled water, and made up to volume.

Standardization of potassium hydroxide is carried out in the same way as for sodium hydroxide (q.v.).

STANDARDIZATION OF BARIUM HYDROXIDE AND AMMONIA

Molecular Weight: 171.38 Ba(OH)₂
Equivalent Weight: 85.69

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Standard solutions of these alkalis are comparatively little used, and are, moreover, extremely hard to keep. The titer will vary from day to day, necessitating re-standardization each time the solution is used.

Preparation and Standardization of Barium Hydroxide

Barium hydroxide, which has been treated with barium chloride to reduce the solubility of barium carbonate, is best used for the standard solution. It must be kept carefully protected from the carbon dioxide of the air, and must be made up with previously boiled distilled water. It is most easily standardized against standard acid, using phenolphthalein as an indicator. (See directions for standardizing sodium hydroxide with hydrochloric acid.)

Preparation and Standardization of Ammonia

Ammonia,²⁴ due to its volatility at ordinary temperatures, is very unsatisfactory as a standard reagent. Weigh, in a closed vessel, the approximate amount of ammonia and transfer quickly to a volumetric flask containing boiled distilled water. Stopper and mix, make up to volume, transfer to tightly stoppered container, and keep in a cool place. Standardize against hydrochloric acid, using methyl orange as an indicator. Methyl red may be preferred, since the transition range is sharper.

²⁴ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

SUPPLEMENTARY REFERENCES

The Stability of Constant Boiling Hydrochloric Acid, J. A. Shaw, *Ind. Eng. Chem.* **18**, 1065 (1926).

The Composition of Hydrochloric Acid of Constant Boiling Point, W. D. Bonner and B. F. Branting, *J. Am. Chem. Soc.* **48**, 3093 (1926).

The Composition of Constant Boiling Hydrochloric Acid at Pressures of 50-1220 millimeters, W. D. Bonner and A. C. Titus, *J. Am. Chem. Soc.* **52**, 633 (1930).

The Boiling Points of Constant Boiling Hydrochloric Acids, W. D. Bonner and R. E. Wallace, *J. Am. Chem. Soc.* **52**, 1747 (1930).

Anhydrous Sodium Carbonate for Standardization, L. Waldbauer, D. C. McCann, and L. F. Tuleen, *Ind. Eng. Chem., Anal. Ed.* **6**, 336 (1934).

Thallous Carbonate as a Titrimetric Standard, R. Hac and K. Kamen, *Collection Czechoslov. Chem. Communications* **4**, 145; cf. *Chem. Listy* **26**, 6 (1932).

Thallous Carbonate as an Acidimetric Standard, Einar Jensen and Bailli Nilssen, *Ind. Eng. Chem., Anal. Ed.* **11**, 508 (1939).

Determination of Sulphur in Rubber Compounds. I. Precipitation of Barium Sulphate in the Presence of Picric Acid, C. H. Lindsly, *Ind. Eng. Chem., Anal. Ed.* **8**, 176 (1936).

Concerning Certain Organic Acids and Acid Anhydrides as Standards on Alkalimetry and Acidimetry, I. K. Phelps and L. H. Weed, *Am. J. Sci.* **26**, 141 (1908); *Chemical Abstracts* **2**, 2659 (1908).

Benzoic Acid as an Acidimetric Standard, G. W. Morey, *J. Am. Chem. Soc.* **34**, 1027 (1912).

Use of Benzoic Acid as an Acidimetric Standard, S. V. Lipin, Z. E. Lukins, S. A. Konovalova, *Trav. inst. metrol. standadisation, U.R.S.S.* No. 5, 59 (in French 68) (1934).

Differential Potentiometric Titration IV: (a) Adaption of the Method of Hydrogen Electrodes, (b) Test of Standards for Precise Acidimetry, D. A. MacInnes and I. A. Cowperthwaite, *J. Am. Chem. Soc.* **53**, 555 (1931).

CHAPTER VI

Standard Solutions of Precipitation Reagents

STANDARDIZATION OF POTASSIUM OR AMMONIUM THIOCYANATE

Molecular Weight:	97.17	KSCN
Equivalent Weight:	97.17	
Molecular Weight:	76.11	NH ₄ SCN
Equivalent Weight:	76.11	

Preparation of Potassium or Ammonium Thiocyanate

The thiocyanates are hygroscopic, and therefore, the theoretical amounts of the salts cannot be weighed with any accuracy. It is necessary to weigh out slightly more than the theoretical. Approximate amounts are weighed out, and made up to one liter. Of the two, ammonium thiocyanate¹ is better adapted for standard solutions.

Recent work by Kolthoff and Lingane² has shown that potassium thiocyanate,¹ when recrystallized and properly dried, is suitable for a primary standard.

¹ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

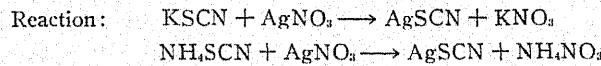
² I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.* 57, 2126 (1935).

Below a relative humidity of 45%, the dried material keeps well, but should be protected from light.

To prepare potassium thiocyanate for a standard solution, the reagent-grade salt may be dried at 150° C for three hours. If excessive moisture causes caking during the first hour of drying, the sample should be removed, the cake broken up by grinding and returned to oven for the remainder of the drying period.

Procedure

Pipette 25 cc of a standard solution of silver nitrate ³ into a 400 cc beaker, and add about 100 cc of distilled water. Now add 5 cc of a saturated solution of ferric ammonium alum ³ acidified with nitric acid, and titrate with the volumetric solution of thiocyanate to the first permanent appearance of a red brown coloration. Samples of silver nitrate of known purity may be titrated in the same manner.



Calculations: Standardization with standard silver nitrate

$$N_{\text{SCN}} = \frac{N_{\text{AgNO}_3} \times V_{\text{AgNO}_3}}{V_{\text{SCN}}}$$

Standardization with solid silver nitrate.
Equiv. Wt. 169.89

$$\text{Normality} = \frac{\text{Wt. of AgNO}_3}{0.16989 \times \text{Titration in cc}}$$

³ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 18, 759 (1926).

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Note: If ferric ammonium alum produces a cloudy solution in water, the addition of a few drops of nitric acid clears the solution. Ferric nitrate may be used in place of ferric alum.

The red brown color observed at the end point of the titration is due to the formation of ferric thiocyanate.

STANDARDIZATION OF SILVER NITRATE

Molecular Weight: 169.89
Equivalent Weight: 169.89

AgNO_3

Preparation of the Solution

Reagent-grade silver nitrate⁴ may be used. This approaches 100% so closely that only a little more than the theoretical amount need be weighed out. The solution should be made up and transferred to a brown bottle as soon as possible. It is essential that the solution be kept free from dust and organic matter, in order to avoid any reduction. With this care, the solution should keep indefinitely.

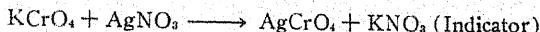
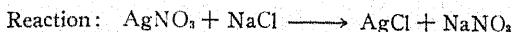
Standardization with Sodium Chloride

Weigh⁵ 0.20–0.25 gm of precipitated sodium chloride and dissolve in 20 cc of distilled water in a casserole or evaporating dish. Add 1.5 cc of a 5% solution of potassium chromate⁶ and titrate to the first permanent tinge of red. Titrate slowly with constant stirring.

⁴ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

⁵ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 20, 979 (1928).

⁶ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem., Anal. Ed.* 1, 171 (1929).



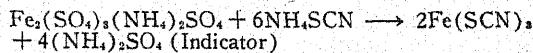
Calculations: The equivalent weight of sodium chloride is 58.45

$$\text{Normality} = \frac{\text{Wt. of NaCl}}{0.05845 \times \text{cc AgNO}_3}$$

Standardization with Ammonium Thiocyanate

Silver nitrate may be standardized against a previously standardized solution of ammonium thiocyanate.

Pipette 25 cc of silver nitrate into a 400 cc beaker containing 200 cc of distilled water and 5 cc of saturated ferric ammonium alum. The solution is titrated with thiocyanate to the first appearance of a permanent red brown color.



Calculations: $N_{\text{AgNO}_3} \times V_{\text{AgNO}_3} = N_{\text{NH}_4\text{SCN}} \times V_{\text{NH}_4\text{SCN}}$

Kolthoff and Lingane⁷ state that potassium thiocyanate, recrystallized from water and dried for a short time at 200° C, can be used for standardizing silver nitrate solution.

Note: Pure sodium chloride may be prepared by passing hydrochloric acid gas, made by allowing concentrated sulphuric acid to drop slowly on solid sodium chloride, into a concentrated salt solution. The pure salt will precipitate. It is filtered on a Büchner funnel and washed with several small portions of distilled water. Dry at 105° C and store in a glass-stoppered bottle. Always dry the sodium chloride for an hour at 105° C before using to standardize silver nitrate solutions.

⁷ I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.* 57, 2126 (1935).

STANDARDIZATION OF POTASSIUM FERROCYANIDE

Molecular Weight: 422.33
Equivalent Weight: 211.17

$K_4Fe(CN)_6 \cdot 3H_2O$

Preparation of the Solution

Weigh out the required amount of the salt and make up to volume. The solution, on standing, oxidizes slightly, forming some ferricyanide. As diphenylamine⁸ and diphenyl benzidine are sometimes used as internal indicators in preference to the outside indicator uranyl nitrate, and are aided by the presence of ferricyanide, the solution is allowed to age for several weeks before standardizing, or a maximum of 150 milligrams of potassium ferricyanide per liter is added, whereupon the solution may be standardized immediately. If either diphenylamine or diphenyl benzidine is used, a 1% solution in concentrated H_2SO_4 is made up, and 0.2 cc used per 100 cc of solution. In using diphenylamine, a titration correction must be applied. Diphenyl benzidine, however, is independent of this correction. The color change is to a deep blue color in both cases. Temperature also affects the sensitivity of these indicators. If uranyl nitrate is used, a 1% solution in water is recommended.

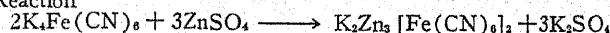
Standardization

Weigh out appropriate samples of pure zinc oxide

⁸ W. H. Cone and L. C. Cady, *J. Am. Chem. Soc.* 49, 356 (1927).

calculated to give titrations of around 40 cc. Dissolve in dilute H_2SO_4 and dilute to 100 cc. Add $(NH_4)_2SO_4$, heat to 60° C and titrate immediately. Do not let the temperature drop below 50° C. If it does, reheat the solution and continue the titration. If an internal indicator is used, the color change is from a light bluish green to a deep blue. In dilute solutions, this change is not evident. In the case of uranyl nitrate, the indicator is spotted on a white porcelain plate. When the end point is approached, the solution should be spotted for every 0.10 cc of ferrocyanide added. A dark brown ring or coloration developing within 2-3 seconds is taken as the end point.

Reaction



The titration is carried out in hot solution because at room temperature, although the above reaction goes to completion, the freshly formed zinc complex reacts with the uranyl nitrate indicator. It is gradually converted to an allotropic form which does not react with the indicator. Heating the solution converts it immediately to this latter phase.

Calculations

Since ferrocyanide is used, for the most part, in the determination of zinc, it is usually evaluated in terms of zinc oxide. In other words, $\frac{Wt. \text{ of } ZnO}{\text{Titration in cc}}$ will represent the titer of the solution. A customary figure of 21.6 gm of potassium ferrocyanide gives approximately 1 cc \approx 0.006 gm zinc oxide.

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SUPPLEMENTARY REFERENCES

Standardization of Silver Nitrate Solutions Used in Chemical Studies of Sea Water, T. G. Thompson, *J. Am. Chem. Soc.* **50**, 681 (1928).
Bartholow Park, *J. Am. Chem. Soc.* **54**, 180 (1932).

CHAPTER VII

Standard Solutions of Oxidizing Reagents

STANDARDIZATION OF IODINE

Atomic Weight: 126.92
Equivalent Weight: 126.92 I₂

Preparation of the Solution

Since there is always a possibility of iodine¹ containing chlorine, bromine, or water as impurities, it is usually advisable to resublimate it. This may be done very simply, using the apparatus shown in Figure 1. The iodine crystals are heated slowly with a very small flame, and the iodine sublimes in crystals on the cooled portion of the water-cooled, round-bottom flask. The sublimed iodine is transferred to a glass-stoppered bottle.

In making standard solutions of iodine, it is necessary to dissolve the iodine in a solution of potassium

¹ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

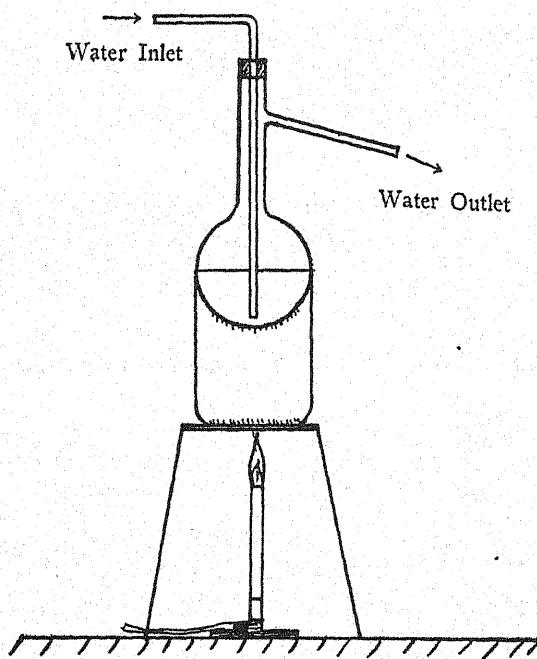


FIG. I

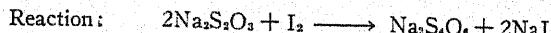
iodide.² Therefore, the following procedure is used in making a 0.1 *N* solution. Weigh accurately 12.692 gm of sublimed iodine into a glass-stoppered tall-form weighing tube. Dissolve 25 gm of potassium iodide in 35-40 cc of water. Uncover the weighing bottle and add about 20 cc of this solution. Swirl gently to dissolve the bulk of the iodine and transfer to a liter

² Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 19, 645 (1927).

volumetric flask. Rinse the weighing tube with the remainder of the iodide solution, quantitatively transferring all of the iodine to the liter flask. Add no water until all the iodine has dissolved. After diluting to volume, transfer to a brown bottle. Iodine solutions are not stable to light, decomposition taking place with the formation of hydriodic acid. A high room temperature also affects them to the point of volatilizing some iodine. Hence, it is necessary to standardize the solutions frequently.

Standardization against 0.1 N Thiosulphate

Aliquots of previously standardized thiosulphate solution are transferred to Erlenmeyer flasks and diluted to 150 cc. The solution is titrated with the iodine to be standardized to a permanent blue end point, using freshly prepared starch as an indicator.



Calculations: $N_{\text{I}_2} \times V_{\text{I}_2} = N_{\text{Na}_2\text{S}_2\text{O}_3} \times V_{\text{Na}_2\text{S}_2\text{O}_3}$

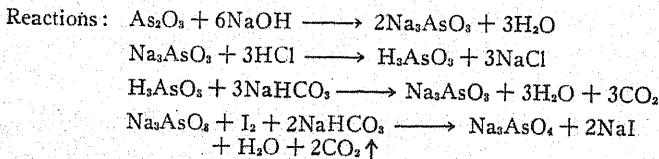
Standardization with Arsenious Oxide

Weigh accurately 0.2000 gm of arsenious oxide,³ which will give a titration of 40 cc, and dissolve in 10 cc of *N* sodium hydroxide. Dilute to 150 cc and add HCl until the solution is faintly acid. Add, cautiously, enough of a concentrated solution of sodium bicarbonate to represent 2-3 gm of the salt. Add starch and titrate to a permanent blue end point. Cover the

³ Obtainable from the U. S. Bureau of Standards.

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beakers with a watch glass while adding the bicarbonate:



The arsenious oxide dissolves more readily in sodium hydroxide than in bicarbonate. The titration, however, must be carried out in a solution alkaline with bicarbonate. It is for this reason that the solution containing an excess of caustic is neutralized with acid.

Calculations: The equivalent weight of arsenious oxide is 49.46

$$\text{Normality} = \frac{\text{Wt. of As}_2\text{O}_3}{0.04946 \times \text{cc Titration}}$$

Recrystallized sodium thiosulphate may be used as a primary standard. It should be kept in a container at a definite humidity, such that only the pentahydrate can exist. A stock solution of arsenious oxide may be prepared by accurately weighing 4.946 gm, dissolving in 40 cc of 1 N NaOH, acidifying with HCl until neutral to litmus, and making up to one liter. Kolthoff⁴ states that a solution made according to these directions is stable over a long period.

Note: The importance of potassium iodide should not be underestimated. It is essential that potassium iodide be present, particu-

⁴ Kolthoff and Furman, *Volumetric Analysis, Vol. I* (1929), 235.

larly in cases where the iodine titration is small; one cc of 10% solution is sufficient for a volume of 200-300 cc. Omission causes consumption of iodine. Potassium iodide is, of course, supplied by the standard solution, but if the probable titration is unknown, it is safer to add more.

The reason for adding the iodide to the standard solution is that it increases the solubility, and decreases the vapor pressure of the iodine, thus reducing the possibility of loss by volatilization.

STANDARDIZATION OF SODIUM THIOSULPHATE

Molecular Weight: 248.19
Equivalent Weight: 248.19

$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

Preparation of the Solution

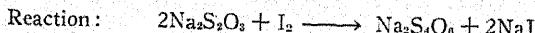
For a 0.1 *N* solution, 24.82 gm are weighed out, dissolved, and made up to one liter. The anhydrous salt should never be used for volumetric solutions because of the uncertainty in its composition. The hydrated salt⁵ is obtainable in a high degree of purity in the market and may be used without further purification. It has been stated that a 0.1 *N* solution can be made by simply weighing accurately the required amount of the salt and diluting to exact volume, but this is not safe practice, since discarding the effect of manual errors and errors due to uncalibrated apparatus, thiosulphate in commercial lots sometimes shows evidence of the presence of the lower hydrates, which are noticeable as a powdery deposit on the surface of the crystals.

⁵ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 18, 759 (1926).

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Standardization with Iodine

A previously standardized solution of iodine may be used. An aliquot is titrated with the thiosulphate. Add starch near the end point and titrate to the disappearance of the blue color. Iodine itself may be used as a primary standard. Sublime the iodine according to the directions given under the *Standardization of Iodine*. Weigh accurately a small weighing tube with a ground glass stopper containing 2-3 gm of potassium iodide in 2-3 cc of water. The heat of solution of potassium iodide is negative, and it is necessary to wait until the weighing tube and solution have attained room temperature before weighing. Now add quickly about 0.5 gm of sublimed iodine and weigh again. The difference is the exact amount of iodine added. The stoppered weighing tube is transferred to a 300 cc Erlenmeyer flask containing 150 cc of distilled water and allowed to open *only under the water*. The solution is now titrated in the usual manner.



$$\text{Calculations: } N_I \times V_I = N_{\text{Na}_2\text{S}_2\text{O}_3} \times V_{\text{Na}_2\text{S}_2\text{O}_3}$$

Iodine has an equivalent weight of 126.92

$$\text{Calculations: Normality} = \frac{\text{Wt. of Iodine}}{0.12692 \times \text{cc Titration}}$$

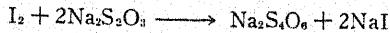
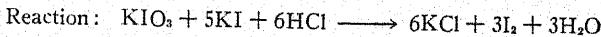
Standardization with Potassium Iodate

Potassium iodate may be purchased in a high state of purity, or the commercial salt may be recrystallized

from water and dried at 180° C. Its great disadvantage is its low equivalent weight: 35.67.

Weigh out 0.15 gm of the salt and dissolve in 50 cc of distilled water. Add 20 cc of a 15% potassium iodide solution. Make the volume up to 150 cc and add 5 cc of concentrated HCl. Titrate immediately. Add starch near the end point and titrate to the disappearance of the blue color.

Note: In all titrations where iodine is liberated, it is best to carry out operations in an Erlenmeyer flask, or stoppered flask, to minimize loss of iodine.



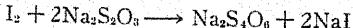
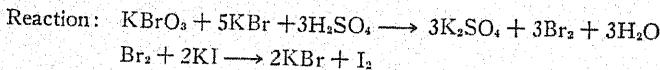
$$\text{Calculations: Normality} = \frac{\text{Wt. of KIO}_3}{0.03567 \times \text{cc Titration}}$$

Standardization with Potassium Bromate

The same disadvantage exists with this salt as with the iodate, namely, its low equivalent weight, which is 27.84. It also has the disadvantage of sometimes containing bromide. This may be tested for, qualitatively, by adding 1-2 cc of 4 N H₂SO₄ to a 1% solution. After five minutes, no color should develop. The bromate-iodide-acid reaction does not take place as quickly as the iodate-iodide-acid. After addition of acid, it is necessary to let the mixture stand for several minutes before proceeding with the titration. Also, the concentration of the acid is an important factor. The following procedure is satisfactory: Weigh 0.12 gm of potas-

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sium bromate into an Erlenmeyer flask, and dissolve in 50 cc of distilled water. Add 20 cc of 15% potassium iodide solution and dilute to 150 cc. Now add 15 cc of 10% H_2SO_4 , stopper the flask, and let stand for three minutes. Titrate, using starch as an indicator.



Calculations: The equivalent weight of $KBrO_3$ is 27.84

$$\text{Normality} = \frac{\text{Wt. of } KBrO_3}{0.02784 \times \text{Titration in cc}}$$

Standardization with Potassium Dichromate^{6, 7, 8}

Potassium dichromate⁹ is another salt which can be obtained in a high degree of purity. Impure dichromate may readily be recrystallized from water and dried at 200° C. Under the right conditions of acidity, potassium dichromate is very satisfactory as a standard substance. The reaction first passes through an induction period and then proceeds at increasing speed. The acidity of the solution, to a great extent, controls the reaction. If, for instance, the acidity is in the neighborhood of 0.5–1.0 normal, it is necessary to let the solution

⁶ W. C. Vosburgh, *J. Am. Chem. Soc.* 44, 2120 (1922).

⁷ H. H. Willard and Philena Young, *J. Ind. Eng. Chem., Anal. Ed.* 7, 57 (1935).

⁸ W. C. Bray and H. E. Miller, *J. Am. Chem. Soc.* 46, 2204 (1924).

⁹ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

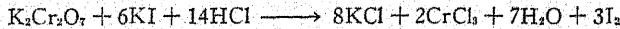
stand for 5 minutes before titrating; but, if the acidity is 1.4 to 1.5 normal, the solution may be titrated immediately. However, the acidity must not be too high, otherwise, the possibility of air oxidation enters, which may lead to erroneous results. It is, therefore, extremely important to adjust the acidity to the right concentration, if correct results are to be obtained.

The practice of weighing out potassium dichromate, diluting to a specific volume, and assuming this to be exactly 0.1 normal, although sufficiently accurate for routine procedure, should not be acceptable for accurate work.

Weigh 0.12–0.15 gm of previously dried dichromate and dissolve in 50 cc of distilled water. Add 15 cc of 15% KI, and 7 cc of concentrated HCl. Titrate immediately and add starch as an indicator. The end point should be observed carefully so as not to overtitrate. The color change is from blue to the green color of chromic salts.

An alternate procedure may be used. Weigh out the sample and dissolve in 75 cc H₂O. Add 15 cc of 15% KI and 10 cc of concentrated HCl. Let stand for 5 minutes in the dark, dilute to 400 cc, and titrate.

Reaction:



Calculations: The equivalent weight of K₂Cr₂O₇ is 49.04

$$\text{Normality} = \frac{\text{Wt. of K}_2\text{Cr}_2\text{O}_7}{0.04904 \times \text{Titration in cc}}$$

Standardization with Copper or a Copper Salt

Copper of known purity, or a pure copper salt may be used as a standard substance. If copper is used, it should first be washed with alcohol and ether, to remove any oily material, polished bright with a suitable cleaner, rinsed with water, and again with alcohol, and finally dried for a short time at 105° C. Dissolve a suitable amount of the copper in 10 cc of 6 *N* H₂SO₄. Dilute to 35 cc with distilled water, add 15 cc of 15% KI, and titrate, using starch as an indicator. If the copper salt is used, dissolve the sample in 35 cc of distilled water, containing 5 cc of 6 *N* H₂SO₄. Add 15 cc of 15% KI, and titrate.

In a recent article, Huerre ¹⁰ states that a large excess of potassium iodide must be present. Loss of CuI is due to the solubility in thiosulphate solution.

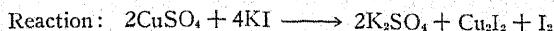
G. Bruhns ¹¹ found that potassium thiocyanate was useful in this titration, reducing the amount of potassium iodide necessary and speeding up the reaction. Kolthoff ¹² gives the following procedure using thiocyanate: 0.5 to 1 cc of *N* KI is added to the acidified copper solution, and then 10 cc of 10% potassium thiocyanate. Cupric thiocyanate is precipitated. The solution is titrated immediately. The dark brown thio-

¹⁰ R. Huerre, *J. Pharm. Chim.* 23, 594 (1936).

¹¹ G. Bruhns, *Chem. Ztg.* 42, 301 (1918).

¹² Kolthoff and Furman, *Volumetric Analysis*, Vol. II (1929), p. 430.

cyanate disappears, while the solution assumes the dark brown color due to iodine. Toward the end, starch is added and the titration continued to a permanent change of iodine-starch blue to leather yellow or dirty violet.



Calculations: The equivalent weight of copper is 63.57, and that of CuSO_4 is 160.63.

$$\text{Normality} = \frac{\text{Wt. of Cu, or CuSO}_4}{\text{Milliequivalent} \times \text{cc Titration}}$$

Note: Much has been written concerning the stability^{13, 14, 15} of thiosulphate solutions. Borax or sodium carbonate may be used as stabilizing agents, 0.1 gm Na_2CO_3 per liter, or 3.8 gm borax per liter. It has been the writer's experience that thiosulphate made up to volume with previously boiled distilled water and kept in clear glass bottles, in the dark, shows no appreciable diminution in titer, after 1-2 months. On the other hand, solutions kept in brown glass bottles gave evidence of deterioration within two weeks. When stabilized with either borax or carbonate, however, they retained their titer for longer periods.

STANDARDIZATION OF POTASSIUM PERMANGANATE

Molecular Weight: 158.03
Equivalent Weight: 31.61

KMnO_4

Preparation of the Solution

Analytical-grade potassium permanganate¹⁶ may be used, or, to insure greater purity, since even the ana-

¹³ F. O. Rice, M. Kilpatrick, and W. Lemkin, *J. Am. Chem. Soc.* **45**, 1361 (1923).

¹⁴ Kolthoff and Furman, *Volumetric Analysis, Vol. I* (1929), p. 231.

¹⁵ Ph. Korkheimer, *Pharm. Ztg.* **80**, 1330 (1935).

¹⁶ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* **18**, 759 (1926).

lytical grade contains impurities, the salt may be recrystallized. Weigh out the required amount and dissolve in distilled water. Let the solution stand on the steam bath for 2-3 hours, or bring to a boil and heat 1 hour on the steam bath. This is necessary, since distilled water usually contains reducing substances. The solution is cooled and filtered either through a Gooch crucible or through a glass filtering funnel of the Büchner type having a porous plate. The manganese dioxide must be removed, since it acts as a catalytic agent, promoting the reduction of the permanganate. Make the filtered solution up to one liter, and transfer to a clean, clear glass bottle. Keep protected from the light. Some reduction will take place and, at intervals, it is necessary to filter off the manganese dioxide. Unless used constantly, it is best to restandardize before making a titration.

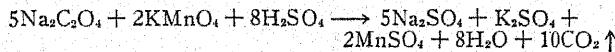
Standardization with Sodium Oxalate or Oxalic Acid

Sodium oxalate or oxalic acid purchased from the U. S. Bureau of Standards is recommended. Weigh out a 0.2-0.3 gm sample and dissolve in 50-60 cc of distilled water. Add 10 cc of 3 N H_2SO_4 , heat to 80° C or a little above, and titrate slowly with permanganate. Do not let the temperature fall below 80° C. The reaction starts very slowly at first, and it is best to add only a few drops of permanganate. When some oxidation has taken place resulting in the formation of manganous salt, the reaction goes rapidly, due to the

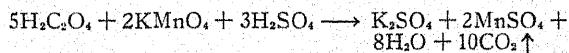
catalytic action of the manganous ions. The solution must be stirred rapidly throughout the determination. The end point is taken as the first permanent pink coloration. In their standardization of permanganate with sodium oxalate, Fowler and Bright¹⁷ correct for this error of overtitration, which they state to be 0.03–0.05 cc.

The presence of hydrochloric acid tends to give high results, due to oxidation of chloride ions to hypochlorous acid.

The reaction of permanganate, which is attended by side reactions, in its simplest form is as follows:



or



Calculations: The equivalent weight of sodium oxalate is 66.995, and that of oxalic acid, with two molecules of water, 63.03

$$\text{Normality} = \frac{\text{Wt. of sample}}{0.067 \text{ (or 0.06303)} \times \text{cc Titration}}$$

Ammonium oxalate,¹⁸ also, has been suggested as a primary standard.

¹⁷ R. M. Fowler & H. A. Bright, *J. Research Nat. Bur. Standards* 15, 493 (1935).

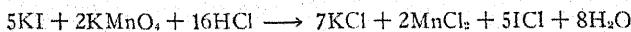
¹⁸ Treadwell and Hall, *Analytical Chemistry*, Vol. II (1930), 513.

¹⁹ M. M. Kirilov, *J. Applied Chem.* 9, 2067 (in French) (1936).



Standardization with Potassium Iodide

The principle of this method depends upon the following equation:



Andrews²⁰ found that potassium iodide could be oxidized quantitatively by various reagents to colorless ICl, and also, that unless the acid concentration was fairly high, hydrolysis of the ICl took place. Kolthoff, Laitinen and Lingane,²¹ who have applied this method to the standardization of permanganate, give the following procedure:

To a glass-stoppered flask containing 25 cc of distilled water and 1 cc of concentrated HCl, add pure potassium bicarbonate to slight excess. A weighed sample of fused potassium iodide is next added, and then sufficient concentrated HCl, assuming a final volume of 350 cc, so that the solution is 3.7–5.5 N with respect to the acid. Cool in an ice bath and add 6 cc CCl₄. Titrate with permanganate to the disappearance of the iodine color in the CCl₄ layer.

$$\text{Calculations: Normality} = \frac{\text{Wt. of KI}}{0.08299 \times \text{cc Titration}}$$

Note: Instead of the fused salt, potassium iodide, which has been dried at 200–220° C, may be used. The results may be slightly higher (0.02–0.03%) due to the retention of occluded water.

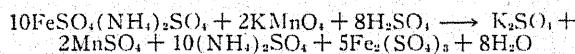
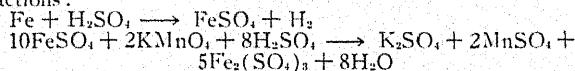
²⁰ L. W. Andrews, *J. Am. Chem. Soc.* **25**, 756 (1903); *Z. anorg. allgem. Chem.* **36**, 76 (1903).

²¹ I. M. Kolthoff, H. A. Laitinen and J. J. Lingane, *J. Am. Chem. Soc.* **59**, 429 (1937).

Standardization with Iron Wire,¹⁸ Ferrous Sulphate, or Mohr's Salt

A suitable quantity of pure iron wire, or either of the two salts is weighed out and dissolved in dilute sulphuric acid. The solution is diluted to approximately 100 cc and run through a Jones reductor, to insure complete reduction of the ion. Add 5 cc of phosphoric acid (85%) and titrate with permanganate to the first permanent pink color. The advantage of adding phosphoric acid is that colorless complex phosphate ions are formed, and the end point is, therefore, sharper, since otherwise it is a reddish orange.

Reactions:



Calculations:

The equivalent weights used are:

$$\text{Fe} = 55.84$$

$$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 278.01$$

$$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} = 391.90$$

$$\text{Normality} = \frac{\text{Wt. of sample}}{\text{Milliequivalent} \times \text{cc Titration}}$$

Pure iron (electrolytic) is available for standardization. Mohr's salt, which has the advantage of a high equivalent weight, is seldom obtainable pure. However, the salt may still be used as a standard, if first its reducing power is determined.

STANDARDIZATION OF POTASSIUM DICHROMATE

Molecular Weight: 294.21
 Equivalent Weight: 49.04

$K_2Cr_2O_7$

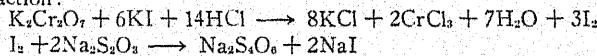
Preparation of the Solution

Potassium dichromate, as previously stated, may be prepared to such a high degree of purity that many authors recommend weighing out the required amount of the salt and making up to volume, without further standardization.

Standardization with 0.1 N Sodium Thiosulphate

Pipette 25 cc of the dichromate solution to be standardized into a 300 cc Erlenmeyer flask. Add 15 cc of 15% KI solution and 7 cc of concentrated HCl. Titrate immediately with thiosulphate, using starch as an indicator. The color change is from blue to the characteristic green of chromic salts. This procedure has been dealt with under the standardization of thiosulphate.

Reaction:



$$\text{Calculations: } N_{K_2Cr_2O_7} \times V_{K_2Cr_2O_7} = N_{Thio} \times V_{Thio}$$

Standardisation with Ferrous Ammonium Sulphate

Potassium dichromate may also be standardized by use of ferrous ammonium sulphate²² as a primary

²² Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* **18**, 759 (1926).

standard. Sufficient amount of the purest obtainable salt is weighed out to give a titration of 35-40 cc. The titration may be carried out with either an outside indicator, potassium ferricyanide, or an internal indicator such as diphenylamine,²³ or diphenylbenzidine.^{24, 25} If ferricyanide is used, a 0.01% solution is spotted on a porcelain plate, the ferrous ammonium sulphate is dissolved in 25 cc of distilled water, 10 cc of dilute H_2SO_4 added; and titrated with potassium dichromate. When the end point is near, the solution is spotted at intervals of 0.1 cc. The end point is reached when no blue color appears on the spot plate after two minutes.

If diphenylamine or diphenylbenzidine is used, it is necessary to add phosphoric acid either at the beginning of the titration or shortly before the true end point is reached. Phosphoric acid is necessary, since if it is not used, the end point is reached too soon, due to the indicator being partially oxidized by ferric ions. Phosphoric acid forms complexes with ferric ions, lowering the oxidation potential of the ferrous-ferric system. An indicator blank should be run, and the titration subtracted from the total titration of the sample.

Dissolve the sample in 25 cc of distilled water, add

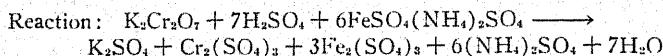
²³ J. Knop, *J. Am. Chem. Soc.* **46**, 263 (1924).

²⁴ H. H. Willard and Philena Young, *J. Ind. Eng. Chem.* **20**, 764 (1928).

²⁵ W. H. Cone and L. C. Cady, *J. Am. Chem. Soc.* **49**, 357 (1927).

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10 cc of dilute H_2SO_4 and 15 cc of sulphuric acid-phosphoric acid mixture (150 cc conc. H_2SO_4 and 160 cc 85% phosphoric acid made up to one liter). Add 2-3 drops of 1% indicator solution (in concentrated H_2SO_4) and titrate. As the end point approaches, the solution turns greenish blue and at the end point suddenly changes to an intense blue color.



Calculations: The equivalent weight of ferrous ammonium sulphate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (Mohr's salt) is 391.90

$$\text{Normality} = \frac{\text{Wt. of sample}}{0.3919 \times \text{net cc Titration}}$$

STANDARDIZATION OF FERROUS AMMONIUM SULPHATE, OR FERROUS SULPHATE

Molecular Weight: 391.90
Equivalent Weight: 391.90

$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Molecular Weight: 278.01
Equivalent Weight: 278.01

$FeSO_4 \cdot 7H_2O$

Preparation of the Solution

Ferrous ammonium sulphate—Mohr's salt—possesses the advantage of a high equivalent weight and the disadvantage in that it often contains small amounts of impurities. This, in spite of its high reacting weight, prevents it from being an ideal primary standard for oxidimetry. However, with regard to a standard solu-

tion of the salt, this does not present any difficulty, since it is only necessary to weigh slightly more than the theoretical amount to compensate for these impurities.

Mohr's salt and ferrous sulphate are subject to air oxidation, and both effloresce. They should be kept in tightly stoppered bottles. To overcome these difficulties, various methods have been used in preparing the pure salts. Kolthoff ²⁶ suggests using ferric ammonium sulphate and reducing the solution with hydrogen sulphide. The crystallized ferrous ammonium sulphate is dried to constant weight over saturated sodium bromide solution. It is also possible to reduce ferric ammonium sulphate in a Jones reductor just before standardization. Kolthoff ²⁷ states that ferric ammonium sulphate weathers readily but is stable at a relative humidity of 70%. Therefore, if this salt is used as a starting point, it is first necessary to allow it to come to equilibrium at 70% relative humidity.

If the commercial salts are used in the preparation of tenth normal solutions, 40 gm of Mohr's salt or 28 gm of ferrous sulphate are weighed, dissolved in 300 cc of distilled water containing 30 cc of concentrated sulphuric acid, and made up to one liter.

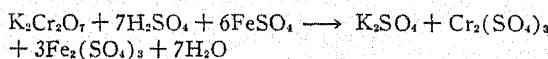
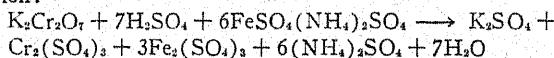
²⁶ I. M. Kolthoff, *Pharm. Weekblad* 61, 561 (1926).

²⁷ Kolthoff and Furman, *Volumetric Analysis, Vol. II* (John Wiley, 1929), 294.

Standardization with Tenth Normal Potassium Dichromate

Pipette 25 cc of freshly prepared solution into a 250 cc Erlenmeyer flask. Add 10 cc of dilute sulphuric acid and 15 cc of sulphuric acid-phosphoric acid mixture (150 cc of conc. sulphuric acid, 160 cc of 85% phosphoric acid made up to one liter). Add 2-3 drops of indicator (1% solution of diphenylamine or diphenylbenzidine in concentrated sulphuric acid) and titrate with standard dichromate to the appearance of a deep blue end point. A blank titration should be run on the indicator and subtracted from the total titration.

Reaction:



$$\text{Calculations: } N_{\text{K}_2\text{Cr}_2\text{O}_7} \times V_{\text{K}_2\text{Cr}_2\text{O}_7} = N_{\text{Mohr's Salt}} \times V_{\text{Mohr's Salt}}$$

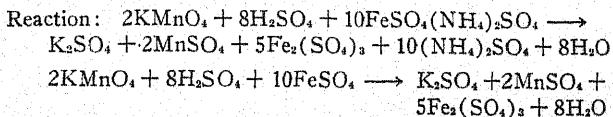
$$N_{\text{K}_2\text{Cr}_2\text{O}_7} \times V_{\text{K}_2\text{Cr}_2\text{O}_7} = N_{\text{FeSO}_4} \times V_{\text{FeSO}_4}$$

Note: The explanation of the use of phosphoric acid is given under the standardization of potassium dichromate.

Standardization with Tenth Normal Potassium Permanganate

Pipette 25 cc of ferrous ammonium sulphate or ferrous sulphate solution into a 250 cc Erlenmeyer flask. Add 25 cc of distilled water, 10 cc of dilute sulphuric acid, and 15 cc of sulphuric acid-phosphoric acid mixture. Titrate with previously standardized

tenth normal permanganate to the appearance of the first permanent pink color.



Calculations: $N_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = N_{\text{Mohr's Salt}} \times V_{\text{Mohr's Salt}}$
 $N_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = N_{\text{FeSO}_4} \times V_{\text{FeSO}_4}$

STANDARDIZATION OF ARSENIOUS OXIDE

Molecular Weight: 197.82 As_2O_3
 Equivalent Weight: 49.46

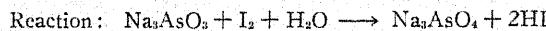
Preparation of the Solution

Arsenic trioxide in pure form may be obtained from the Bureau of Standards. Weigh out 4.946 gm of arsenious oxide and dissolve in 250 cc of distilled water, containing 50 cc of normal sodium hydroxide. When solution has taken place, add enough acid, either hydrochloric or sulphuric, until the solution is neutral or faintly acid. Other methods dissolve arsenic trioxide in water containing sodium carbonate. The control of the final *pH* is important, since if the solution is too alkaline, the arsenite is more or less easily oxidized to arsenate, which naturally affects the titer. Tannanaev²⁸ states, however, that if the *pH* is kept between 7 and 9, the solution will keep indefinitely.

²⁸ N. A. Tannanaev, *Ukrainskii Khem. Zhurnal* 5, Sci. Pt. 217 (1930); *Chemical Abstracts* 25, 2070 (1931).

Standardization with Iodine

Pipette 25 cc of solution into an Erlenmeyer flask containing 25 cc of distilled water in which 1 gm of sodium bicarbonate has been dissolved. Titrate with standard iodine to the appearance of a blue color, using starch as an indicator. Sodium bicarbonate keeps the *pH* of the solution at about 8.36.



$$\text{Calculations: } N_{\text{As}_2\text{O}_3} \times V_{\text{As}_2\text{O}_3} = N_{\text{I}_2} \times V_{\text{I}_2}$$

STANDARDIZATION OF POTASSIUM BROMATE

Molecular Weight: 167.02
Equivalent Weight: 27.84

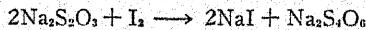
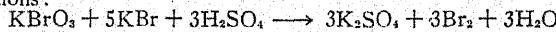
KBrO₃*Preparation of the Solution*

Weigh out 2.784 gm of potassium bromate, previously dried at 150° C, dissolve in a small quantity of distilled water, and dilute to one liter.

Standardization with 0.1 N Sodium Thiosulphate

Pipette 25 cc of the bromate solution into a glass-stoppered bottle or iodine flask and add 20 cc of 10% sulphuric acid saturated with potassium bromide. Re-stopper the flask quickly and let stand for two minutes. Now add 5 cc of saturated potassium iodide solution, let stand one minute and titrate with *N*/10 sodium thiosulphate, using starch as an indicator.

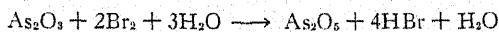
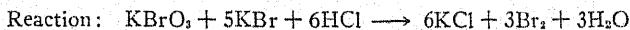
Reactions:



$$\text{Calculations: } N_{\text{KBrO}_3} \times V_{\text{KBrO}_3} = N_{\text{Thio}} \times V_{\text{Thio}}$$

Standardization with Arsenious Acid

Pipette 25 cc of standard arsenious oxide into a 300 cc Erlenmeyer flask, add 30 cc of 1:1 hydrochloric acid and 0.5 gm of potassium bromide. Add 1-2 drops of methyl orange. Titrate with the bromate solution, constantly agitating the flask. The end point is approached slowly. The color change is from red to colorless or pale yellow. The indicator change is due to bleaching of the compound by free bromine.

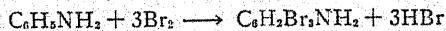
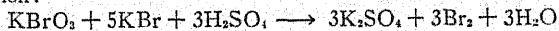


$$\text{Calculations: } N_{\text{KBrO}_3} \times V_{\text{KBrO}_3} = N_{\text{As}_2\text{O}_3} \times V_{\text{As}_2\text{O}_3}$$

Standardisation with Aniline

Aniline may be used as a standard for potassium bromate. Its reaction is similar to phenol, in that it forms a tri-brom compound. An appropriate quantity of freshly distilled aniline is weighed out and transferred to a glass-stoppered iodine flask containing 20 cc of 10% sulphuric acid saturated with potassium bromide. Add 50 cc of bromate solution, and let stand for five minutes. Now add 5 cc of saturated potassium iodide solution, let stand one minute, and titrate the iodine with sodium thiosulphate, using starch as an indicator.

Reaction:



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Calculations: The equivalent weight of aniline is 15.50

$$\text{Normality} = \frac{\text{Wt. of aniline}}{0.0155 \times \text{net cc of KBrO}_3}$$

Note: Potassium bromate solution is sometimes made up with potassium bromide. In this case, 50 gm of bromide are added per liter.

STANDARDIZATION OF POTASSIUM IODATE

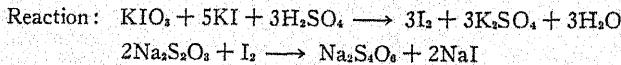
Molecular Weight: 214.03 KIO_3
Equivalent Weight: 35.67

Preparation of the Solution

Potassium iodate may be obtained pure by recrystallization from water. After drying at 180° C, the exact equivalent weight may be accurately weighed out, and made up to volume. However, to avoid any uncertainty as to the purity of the potassium iodate, it is best to standardize the solution.

Standardization with Sodium Thiosulphate

Pipette 25 cc of potassium iodate into a glass-stoppered flask containing 20 cc of 10% sulphuric acid and 5 cc of saturated potassium iodide solution. The reaction proceeds rapidly, and the solution may be titrated, immediately, with standard thiosulphate solution, using starch as an indicator.

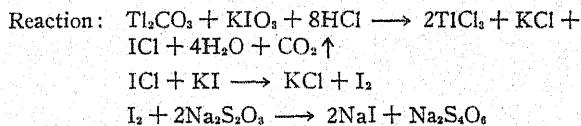


Calculations: $N_{\text{KIO}_3} \times V_{\text{KIO}_3} = N_{\text{Thio}} \times V_{\text{Thio}}$

Standardization with Thallous Carbonate

Berry²⁹ has suggested the use of thallous carbonate as a primary standard for iodate solutions.

Weigh out 0.4–0.5 gm of the salt, dissolve in distilled water, and make strongly acid with concentrated HCl. Add 15 cc of saturated KI solution, and titrate the liberated iodine, using starch as an indicator.



Calculations: The equivalent weight of Tl_2CO_3 is 117.2

$$\text{Normality} = \frac{\text{Wt. Tl}_2\text{CO}_3}{0.1172 \times \text{cc Titration}}$$

STANDARDIZATION OF CERIC SULPHATE

Ceric sulphate is a powerful oxidizing agent, and has been offered as a substitute for permanganate in oxidation reactions. There are numerous advantages, chief among which is the comparative stability³⁰ of ceric sulphate solutions and the fact that there is no decomposition when oxidations with excess sulphate are carried out at boiling temperatures.

Ceric sulphate, as received from chemical supply

²⁹ A. J. Berry, *Analyst* 64, 27 (1939).

³⁰ N. H. Furman, *J. Am. Chem. Soc.* 50, 755 (1928).

houses, averages around 50% as ceric sulphate, the variation being due to the presence of rare earths as impurities, and the fact that the salt is not completely anhydrous. Ceric ammonium sulphate,



whose purity is around 80%, is also used in place of anhydrous ceric sulphate.

Preparation of the Solution

Allowing the ceric sulphate to be 50%, weigh out a little more than twice the equivalent weight, or 67 gm for a tenth normal solution. Add 100 cc of water and 30 cc of concentrated H_2SO_4 . Let the solution stand until the salt is dissolved, adding more water or heating, if necessary. Make up to one liter. The solution will be approximately tenth normal in ceric sulphate and one normal in sulphuric acid.

If ceric ammonium sulphate ($2\text{H}_2\text{O}$) is used, weigh out an equivalent quantity of the salt, depending upon its purity, and dissolve in the same manner as for ceric sulphate. Standard solutions of ceric sulphate may also be prepared by dissolving the oxide, CeO ,³¹ in dilute sulphuric acid.

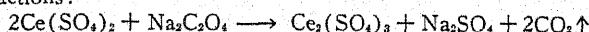
Standardisation with Oxalic Acid or Sodium Oxalate

Weigh out 0.25–0.30 gm of oxalate and dissolve in 100 cc of distilled water. Add 10 cc of 1:1 H_2SO_4 . Heat to 90–95° C and titrate with the ceric sulphate

³¹ H. H. Willard and Philena Young, *J. Am. Chem. Soc.* 50, 1322 (1928).

solution. The solution may be titrated using the ceric sulphate as an indicator, the end point being taken as the first permanent yellow tinge. Orthoferrous-phenanthroline^{32, 33, 34, 35} is a very satisfactory indicator. One drop of the indicator solution is added. The color change is from pink to blue.

Reactions:



Wt. of oxalate

$$\text{Calculations: Normality} = \frac{\text{Wt. of oxalate}}{0.067 \times \text{cc Titration}} \quad \text{or}$$

$$\text{Normality} = \frac{\text{Wt. of oxalic acid}}{0.06303 \times \text{cc Titration}}$$

Standardization with Arsenious Oxide

Either a standard solution of tenth normal arsenite or pure arsenic trioxide (obtainable from the Bureau of Standards) may be used. If the dry salt is used, weigh 0.20 gm samples and dissolve in a few cubic centimeters of normal sodium hydroxide. If a previously standardized solution of arsenite is used, pipette

³² G. H. Walden, L. P. Hammett, and R. P. Chapman, *J. Am. Chem. Soc.* 53, 3908 (1931).

³³ Monograph, Ortho-phenanthroline, published by The G. Frederick Smith Chemical Co., 857 McKinley Ave., Columbus, Ohio, P. O. Box 2611, Station D.

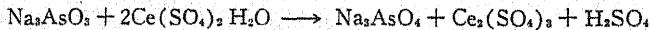
³⁴ A. U. Kirsanov and U. M. Cherkasou, *Zavodskaya Lab.* 5, 143; *Bull. Soc. Chem. (5)*, 3, 817; *Chemical Abstracts* 30, 4779 (1936).

³⁵ H. H. Willard and Philena Young, *J. Am. Chem. Soc.* 55, 3260 (1933).

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25 cc into an Erlenmeyer flask. Either sulphuric or hydrochloric acid may be added. The solution must be strongly acid, otherwise cerous sulphate will precipitate, since it is not very soluble in dilute acid. Add 50–75 cc of distilled water and 20–25 cc of concentrated hydrochloric acid or an equivalent amount of sulphuric acid. If the reagent itself is used as the indicator, the solution, as previously stated, must be heated to around 100° C, since the intensity of color is much greater when hot, making the end point easier to observe. Also, in the absence of a catalyst such as iodine monochloride³⁶ or osmium tetroxide, the solution must be heated to promote a fast reaction. Ortho-phenanthroline ferrous complex may be used as an indicator, one drop of a 0.025% solution being sufficient.

Reaction:



$$\text{Calculations: Normality} = \frac{\text{Wt. of As}_2\text{O}_3}{0.04946 \times \text{cc Titration}}$$

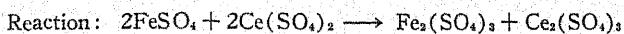
$$\text{or } N_{\text{Ce}(\text{SO}_4)_2} \times V_{\text{Ce}(\text{SO}_4)_2} = N_{\text{As}_2\text{O}_3} \times V_{\text{As}_2\text{O}_3}$$

Standardization with Mohr's Salt or Ferrous Sulphate

Make an approximately tenth normal solution of either Mohr's salt or ferrous sulphate, and determine its strength by titration with a standard solution of potassium dichromate. This is necessary, since the composition of either salt cannot be depended upon.

³⁶ E. H. Swift and C. H. Gregory, *J. Am. Chem. Soc.* 52, 901 (1930).

Having determined the exact strength of the iron solution, pipette 25 cc into an Erlenmeyer flask, and make the volume up to 100 cc. Add 10 cc of 1:1 sulphuric acid, and titrate with ceric sulphate, using ortho-phenanthroline ferrous complex.



$$\text{Calculations: } N_{\text{Ce}(\text{SO}_4)_2} \times V_{\text{Ce}(\text{SO}_4)_2} = N_{\text{FeSO}_4} \times V_{\text{FeSO}_4}$$

SUPPLEMENTARY REFERENCES

Potassium Dichromate as a Standard in Iodimetry and the Determination of Chromates by the Iodide Method, W. C. Vosburgh, *J. Am. Chem. Soc.* **44**, 2120 (1922).

Standardization of Solutions Used in Iodimetry I, S. Popoff and F. L. Chambers, *J. Am. Chem. Soc.* **45**, 1358 (1923).

Standardization of Solutions Used in Iodimetry II, S. Popoff and J. L. Whitman, *J. Am. Chem. Soc.* **47**, 2259 (1925).

Applications of Ceric Sulphate in Volumetric Analysis IX. The Standardization of Thiosulphate Solutions, N. H. Furman and J. H. Wallace, *J. Am. Chem. Soc.* **53**, 1283 (1931).

Employment of Potassium Ferrocyanide in Standardization of Dilute Potassium Permanganate, E. J. deBeer and Axel M. Hjort, *J. Ind. Eng. Chem., Anal. Ed.* **7**, 120 (1935).

The Preparation and Preservation of Standard Potassium Permanganate Solution, Takio Kato, *J. Chem. Soc. Japan* **48**, 408 (1927); *Chemical Abstracts* **22**, 1932 (1928).

The use of Bromate in Titrations with Special Reference to the Indicator Question, Oscar Collenburg, *Tids. Kjemi Bergvesen* **5**, 220, 239 (1925); *Chemical Abstracts* **20**, 883 (1925).

The Preparation of Standard Solutions of Potassium Bromate, Morris L. Yakowitz, *J. Assoc. Official Agr. Chem.* **18**, 505 (1935).

Analysis of Feldspar, Method for Determining Normalities of Potassium Bromate and Sodium Thiosulphate in the Knowles-Redmond Volumetric Procedure for Alumina, E. W. Koenig, *J. Am. Ceram. Soc.* **19**, 257 (1936).

Volumetric Iodate Methods, Jamieson, Chemical Catalog Co.

Use of Indicators, H. H. Willard and Philena Young, *J. Am. Chem. Soc.* **55**, 3260 (1933).

Preparation and Stability of Solutions IX, H. H. Willard and Philena Young, *J. Am. Chem. Soc.* **51**, 149 (1929).

Experiments on Quantitative Oxidation with Ceric Sulphate, A. J. Berry, *Analyst*, August (1929).

CHAPTER VIII

Miscellaneous Standard Solutions

UNDER this heading are grouped several solutions whose practical importance in the analytical laboratory—with the exception of Wijs and Hanus solutions—is slight. However, since they are used to some extent, they have been included in the list of standard solutions.

STANDARDIZATION OF WIJS' OR HANUS' SOLUTION

Both of these solutions are used to determine unsaturation in organic compounds. The active constituent of Wijs' solution is iodine monochloride, and that of Hanus' solution is iodine monobromide. Glacial acetic acid is used as the solvent. There is no necessity for the solutions to contain exact equivalents.

Preparation of the Solution

Weigh out approximately 12.7 gm of iodine, and dissolve in several hundred cubic centimeters of glacial acetic acid. The iodine will dissolve readily in the acetic acid, if it has been ground to a fine powder in a

mortar. Gentle heating in a covered flask will facilitate solution, but prolonged heating will result in an appreciable loss of iodine. When the iodine is in complete solution, an equivalent (approximately) of chlorine or bromine is added. In the case of Wijs' solution, chlorine is bubbled slowly into the solution until the color begins to change and becomes definitely lighter. Caution: iodine must always be in excess, and the final color should be a deep red brown. A little experience will dictate the approximate point at which to stop.

Hanus' solution is prepared by adding 6.6 cc of bromine (not bromine water) to the acetic acid solution of iodine. Both solutions are now approximately 0.2 normal with respect to the iodine, since iodine, chlorine, and bromine are all equivalent to each other. Keep the solutions in brown bottles and store in a cupboard. Even under these conditions, the solutions will change their titer.

Standardisation of the Solution

It is not necessary to standardize the solution, but its strength in terms of tenth normal thiosulphate is usually determined.

Pipette 25 cc of either Wijs' or Hanus' solution into a 250 cc Erlenmeyer flask, add 15 cc of 15% potassium iodide, and titrate with thiosulphate, using starch as an indicator, to the disappearance of the blue color. Record this titer as the strength of the solution. In running determinations of iodine values, it is always

necessary to include a blank, since, as stated above, the titer will change over a period of time.

STANDARDIZATION OF IODINE THIOCYANATE SOLUTION

Iodine thiocyanate is also used to determine unsaturation in organic compounds. The solution is stable for a comparatively short time, and should be kept in the dark.

Preparation of the Solution

To 900 cc of C.P. benzol, add 50 cc of acetic anhydride and 50 cc of glacial acetic acid. Allow to stand in a dry, glass-stoppered bottle, in the dark for eight days. Add 15 gm of lead thiocyanate and 2 cc of liquid bromine. Shake vigorously, at frequent intervals, until the solution has become decolorized. During this period, keep the solution in the dark or away from any source of bright light. After the solution is decolorized, add 4-6 gm of iodine. As soon as the iodine dissolves, filter the solution rapidly into a dry, glass-stoppered bottle and store in the dark.

Standardization of the Solution

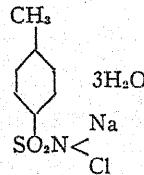
The strength of the solution is determined by titration with tenth normal thiosulphate.

Pipette 25 cc of the solution into a glass-stoppered iodine flask. Add quickly 15 cc of 15% potassium iodide, shake vigorously, and titrate the liberated iodine with tenth normal thiosulphate, using starch as an

indicator. A blank determination must always be run when determining unsaturation.

STANDARDIZATION OF CHLORAMINE T

Molecular Weight: 281.5
Equivalent Weight: 140.75



Chloramine T—tolamine, activin—is the sodium salt of p-toluene sulphonchloroamide. Its use as a volumetric reagent^{1, 2, 3, 4} was suggested by Noll.^{5, 6} In its action, chloramine T resembles the hypochlorites and reacts in oxidation reactions similar to iodine. It has been used in determination of sulphites, arsenic, antimony, tin, and iron.

¹ E. Jungmichl and J. Hackl, *Melliand Textilber.* 7, 850 (1926).

² O. Tomicek and B. Sucharda, *Casopis Ceskoslov. Lekarnictva* 11, 285, 309 (1931); *Chemical Abstracts* 26, 1210 (1932).

³ M. Markees, *Pharm. Acta Helv.* 6, 106 (1931).

⁴ A. S. Komarovskii, Vera Feodorovna Filanova, and I. M. Korenman, *J. Applied Chem. (U.S.S.R.)* 6, 742 (1933); *Z. Anal. Chem.* 96, 321 (1934).

⁵ A. Noll, *Papier Fabr. Tech. Wiss. Teil* 22, 385; *Zellstoff u. Papier* 4, 218 (1924); *Chemical Abstracts* 19, 176 (1925).

⁶ A. Noll, *Chem. Ztg.* 48, 845 (1924).

Preparation of the Solution

Since the purity of the commercial product may vary, approximately 15 gm are dissolved in water and made up to one liter (actually 14.1 gm represent one equivalent). If there are any doubts as to the purity, the salt may be recrystallized from water. The solution is stable,^{7,8} if kept in brown bottles.

Standardization with Arsenious Acid

Standardization may be made either with the dry salt or with a previously standardized solution of arsenious acid. Pipette 25 cc of tenth normal arsenious acid into an Erlenmeyer flask. Add 2-3 cc of a 10% solution of potassium iodide (or a small crystal), 5 cc of starch solution, and titrate to the first appearance of a blue color.

$$\text{Calculations: } N_{\text{Chlor.}} \times V_{\text{Chlor.}} = N_{\text{As}_2\text{O}_3} \times V_{\text{As}_2\text{O}_3}$$

$$\text{or } \text{Normality} = \frac{\text{Wt. of As}_2\text{O}_3}{0.04946 \times \text{cc Titration}}$$

STANDARDIZATION OF HYPOCHLORITE SOLUTIONS

Hypochlorites and hypobromites are powerful oxidizing agents and useful in oxidation reactions that are carried out in alkaline or neutral solution. Kolthoff and Stenger⁹ have proposed the use of calcium hypo-

⁷ Julius Bebie, *J. Am. Pharm. Assoc.* 9, 974 (1920).

⁸ Bernard Salkin, *J. Am. Pharm. Assoc.* 13, 613 (1924).

⁹ I. M. Kolthoff and V. A. Stenger, *Ind. Eng. Chem., Anal. Ed.* 7, 79 (1935).

chlorite as a standard reagent, since this compound is much more stable than the alkali hypochlorites. It may be obtained from the Mathieson Alkali Co., 60 East 42nd Street, New York City, under the code letters CCH.

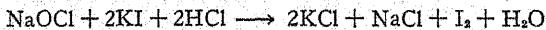
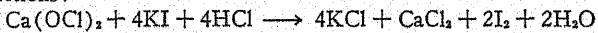
Preparation of the Solution

Determine the available chlorine in the sample and weigh out enough to make a tenth normal solution when diluted to one liter. Store in a brown bottle, tightly stoppered. It will be necessary to recheck the titer of the solution, particularly if considerable time has elapsed since the solution was last used.

Standardization with Sodium Thiosulphate

Pipette 25 cc of the hypochlorite into an Erlenmeyer flask, and add 15 cc of a 15% solution of potassium iodide. Make up the volume to approximately 100 cc with distilled water, add 10 cc of concentrated hydrochloric acid, and titrate with thiosulphate to the disappearance of the blue color, using starch as an indicator.

Reactions:



Mol. Wt.

Equivalent weight in either case: $\frac{2}{2}$

Calculations: $N_{\text{OCl}} \times V_{\text{OCl}} = N_{\text{Thio}} \times V_{\text{Thio}}$

Standardization with Arsenious Acid

Pipette 25 cc of the hypochlorite solution into a

250 cc Erlenmeyer flask. Add 50 cc of a tenth normal solution of arsenious acid. Titrate the excess arsenious acid with tenth normal iodine to the appearance of the blue starch-iodine color.

Calculations: Calculate the net cubic centimeters of arsenious acid used, then.

$$N_{OCl} \times V_{OCl} = N_{As_2O_3} \times V_{As_2O_3}$$

A more recent addition to this type of standard oxidizing solution is the use of sodium chlorite as a volumetric oxidizing agent. Jackson and Parsons¹⁰ have prepared and used it successfully for the determination of sulphurous acid and sulphites.

STANDARDIZATION OF SODIUM CHLORITE

Preparation of the Solution

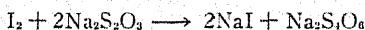
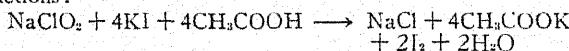
Sodium chlorite is obtainable as a white crystalline solid, very soluble in water, slightly hygroscopic, and about 98% pure, the impurities consisting of sodium chloride, sodium chlorate, and water. The solution is stable over a period of several months, if kept in the dark. Weigh out the required amount of the salt, dissolve in distilled water, and make up to volume.

¹⁰ D. T. Jackson and J. L. Parsons, *Ind. Eng. Chem., Anal. Ed.*, **9**, 14 (1937).

Standardization with Sodium Thiosulphate

Pipette 25 cc of the solution into an Erlenmeyer flask containing 75 cc of distilled water, 15 cc of 10% KI and 15 cc of 30% acetic acid. Titrate the liberated iodine with previously standardized thiosulphate solution, using starch as an indicator.

Reactions :



**STANDARDIZATION OF TITANIUM TRICHLORIDE
OR SULPHATE**

Molecular Weight: 154.27

TiCl_3

Equivalent Weight: 154.27

Molecular Weight: 383.98

$\text{Ti}_2(\text{SO}_4)_3$

Equivalent Weight: 383.98

Titanous salts are powerful reducing agents. As they are affected by air, the solutions are relatively unstable and must be kept under some inert gas. This necessitates special apparatus.¹¹ For isolated analyses, titanous solutions are not recommended. They find their usefulness, however, in routine work, where numerous determinations of the same sort are being run daily.

Preparation of the Solution

Concentrated solutions of the salts may be purchased.

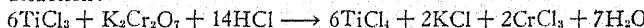
¹¹ W. M. Thornton, Jr. and A. E. Ward, *J. Ind. Eng. Chem.* 19, 150 (1927).

From the strength of the solution, the volume which will contain an equivalent weight can be calculated. This is diluted with freshly boiled distilled water containing three per cent of concentrated hydrochloric acid (or equivalent of conc. H_2SO_4).

*Standardisation with Potassium Dichromate*¹¹

Pipette 25 cc of tenth normal dichromate into a 250 cc Erlenmeyer flask containing 50 cc of boiled distilled water and 5 cc of concentrated hydrochloric acid. Add several drops of diphenylamine as an indicator. Bubble carbon dioxide through the solution continuously and titrate with the titanous solution to an end point.

Reaction:



$$\text{Calculations: } N_{TiCl_3} \times V_{TiCl_3} = N_{K_2Cr_2O_7} \times V_{K_2Cr_2O_7}$$

If the dry salt was used, then,

$$\text{Normality} = \frac{\text{Wt. of } K_2Cr_2O_7}{0.04903 \times \text{cc Titration}}$$

Equivalent weight of $K_2Cr_2O_7$ = 49.03

Note: The solution may also be standardized by titrating a sample of ferric ammonium sulphate (ferric alum), using 10 cc of 15% potassium thiocyanate as an indicator and titrating to the disappearance of the red ferric thiocyanate color. Follow the general directions as outlined under *Standardization*.

STANDARDIZATION OF MANGANIC SULPHATE

Molecular Weight: 398.04

$Mn_2(SO_4)_3$

Equivalent Weight: 398.04

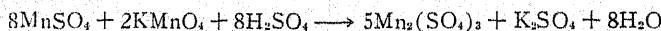
The use of manganic sulphate¹² as a standard re-

¹² A. R. Ubbelohde, *J. Chem. Soc.* 1605 (1935).

agent, in place of permanganate, presents interesting possibilities. Certain difficulties attendant to permanganate titration, such as the presence of chlorides, are overcome by manganic sulphate. A. R. Ubbelohde¹² states that satisfactory results have been obtained in the estimation of nitrites, oxalates, vanadium salts and hydrogen peroxide, and that rapid and satisfactory end points can be obtained without difficulty in the presence of chlorides.

Preparation of the Solution

According to Ubbelohde, a tenth normal solution may be prepared from manganous sulphate in the following manner, and according to the equation:

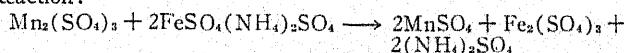


Dissolve 15.10 gm of manganous sulphate in 6 *N* H_2SO_4 , and make up to a liter with 6 *N* H_2SO_4 , keeping the solution cool. Now add 12 cc of *N*/2 KMnO_4 , 2 cc at a time, at intervals of three minutes. A further 2 cc of concentrated H_2SO_4 were added after 8 cc and 12 cc of the KMnO_4 solution, and the solution stored four hours in the dark before use. With these precautions, the reaction proceeds smoothly. If larger volumes are required, special precautions must be taken for cooling the solution to prevent formation of precipitates of the higher oxides. This solution is stable at room temperature, but on dilution, unless the acid concentration is increased, hydrolysis will take place.

Standardization with Ferrous Ammonium Sulphate

Weigh out the necessary amount of ferrous ammonium sulphate and dissolve in 25 cc of distilled water. Add 10 cc of dilute H_2SO_4 and titrate. One drop excess of the reagent gives a definite pink color, which is greatly improved by addition of two drops of glacial phosphoric acid.

Reaction:



$$\text{Calculations: Normality} = \frac{\text{Wt. of } FeSO_4(NH_4)_2SO_4}{0.39804 \times \text{cc Titration}}$$

SUPPLEMENTARY REFERENCES

Calcium Chlorite as a Volumetric Oxidizing Agent, G. R. Levi, *Ind. Eng. Chem., Anal. Ed.* 9, 250 (1937).

See also J. L. Parsons, *Ind. Eng. Chem., Anal. Ed.* 9, 250 (1937).

Oxidation of Amino Acids and of Related Substances with Chloramine, T. D. Dakin, *Biochem. J.* 11, 79 (1917).

Chloramine, P. N. Van Eck, *Pharm. Weekblad* 63, 1117 (1926).

Oxidizing Action of Chloramine, T. G. Schiemann and P. Novak, *Z. Angew. Chem.* 40, 1032 (1927).

The Oxidizing Power of Chloramines, J. Koetschet, P. Koetschet, and Pierre Viaud, *Helv. Chem. Acta* 13, 587 (1930).

Calcium Chlorite as a Volumetric Oxidizing Agent, G. R. Levi, *Ind. Eng. Chem., Anal. Ed.* 9, 250 (1937).

J. L. Parsons, *Ind. Eng. Chem., Anal. Ed.* 9, 250 (1937).

Electrometric Standardization of Titanous Solution, W. S. Hendrixson and L. M. Verbeck, *J. Am. Chem. Soc.* 44, 2382 (1922).

Standardizing Titanous Chloride Solutions and Potentiometric Titration of Copper, E. Zintl and A. Rauch, *Z. Anorg. Allgem. Chem.* 146, 281 (1925).

Application of Titanous Chloride to Potentiometric Titrations, I. M. Kolthoff and O. Tomicek, *Rec. Trav. Chem.* 43, 768 (1924).

Applied Inorganic Analysis, Hillebrand and Lundell (1929), 308.

Stock Solutions of Indicators

ACID-BASE

Phenolphthalein: One gram dissolved in one liter of 50% alcohol. Alcohol is always faintly acid and must be first neutralized with 0.1*N* caustic before adding the indicator.

Methyl Orange: One gram dissolved in one liter of distilled water.

Methyl Yellow: 0.1% in alcohol.

Methyl Red: 0.1% in alcohol.

Thymol Blue: 0.1% in alcohol.

OXIDATION-REDUCTION

Diphenylamine: 1% in conc. H_2SO_4 .

Diphenylbenzidine: 1% in conc. H_2SO_4 .

Ferrous *o*-phenanthroline: can be purchased* ready for use.

* The G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio. P.O.B. 2611—Station D.

PRECIPITATION

Ferric Ammonium Sulphate: Saturated solution in water. Enough concentrated HNO_3 added to clear the solution.

Ferric Nitrate: 10% solution in water.

Potassium Chromate: 5% solution in water.

Uranyl Acetate: 1% solution in water.

STOCK SOLUTIONS OF LABORATORY REAGENTS

Concentrated Acids

Sulphuric acid	— 36 Normal
Hydrochloric acid	— 12 Normal
Nitric acid	— 16 Normal
Acetic acid	— 17.5 Normal
Hydrofluoric acid	— 48%
Aqua regia	— Mix 3 vols. of conc. HCl and 1 vol. conc. HNO_3 just before using.

Dilute Acids

Sulphuric acid	— 18 Normal. Dilute 460 cc of concentrated acid with 540 cc of distilled water.
Sulphuric acid	— 6 Normal. Dilute 1 vol. of concentrated acid with 5 vols. of distilled water.
Hydrochloric acid	— 6 Normal. Mix equal volumes of concentrated acid and distilled water.

Nitric acid	— 6 Normal. Dilute 380 cc of concentrated acid with 620 cc of distilled water.
Perchloric acid	— 2 Normal. Dilute 220 cc of 60% acid with 780 cc of distilled water.
Acetic acid	— 6 Normal. Dilute 350 cc of glacial acetic acid to one liter with distilled water.

Bases

Ammonium hydroxide	— 15 Normal. Concentrated. 6 Normal. Dilute 400 cc of concentrated ammonia with 600 cc of distilled water.
Sodium hydroxide	— 35%. Dissolve one pound of pellet caustic in 748 cc of distilled water.
Sodium hydroxide	— 5 Normal. Dissolve 220 gm in distilled water and make up to one liter.
Potassium hydroxide	— 5 Normal. Contains 312 gm per liter.

Miscellaneous Solutions

Ammonium chloride	— 5 Normal. Contains 268 gm per liter.
Ammonium nitrate	— Normal. Contains 80 gm per liter.

Ammonium oxalate — 0.5 Normal. Contains 36 gm per liter.

Barium chloride — 10%. 100 gm dissolved in 900 cc of distilled water.

Picric acid — Saturated solution in distilled water.

Potassium iodide — 15%. 150 gm dissolved in 850 cc of distilled water.

Silver nitrate — 10%. 100 gm dissolved in 900 cc of distilled water.

Sodium carbonate — 3 Normal. 159 gm per liter.

Stannous chloride — Normal. 113 gm of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ per liter. The solution is made acid by addition of a few cubic centimeters of conc. HCl. To keep the solution reduced, strips of metallic tin should be added.

NORMAL SOLUTIONS OF ACIDS AND BASES

Compound	Formula	Molecular Weight	Normal Solution Contains gm/l	Milli-Equivalent gm/cc
Acetic Acid	CH ₃ COOH	60.03	60.03	0.06003
Boric Acid	H ₃ BO ₃	61.84	61.84	0.06184
Hydrobromic Acid	HBr	80.92	80.92	0.08092
Hydrochloric Acid	HCl	36.46	36.46	0.03646
Oxalic Acid	H ₂ C ₂ O ₄	126.05	53.03	0.05303
Phosphoric Acid	H ₃ PO ₄	98.04	32.68	0.04902
Sulphuric Acid	H ₂ SO ₄	98.08	49.04	0.04904
Ammonium Hydroxide	NH ₄ OH	17.03	17.03	0.01703
Barium Hydroxide	Ba(OH) ₂ ·8H ₂ O	315.50	157.75	0.15775
Calcium Hydroxide	Ca(OH) ₂	74.09	37.05	0.03705
Potassium Hydroxide	KOH	56.1	56.1	0.0561
Potassium Carbonate	K ₂ CO ₃	138.20	69.10	0.06910
Sodium Carbonate	Na ₂ CO ₃	106.00	53.00	0.05300
Sodium Hydroxide	NaOH	40.00	40.00	0.04000
Sodium Tetraborate	Na ₂ B ₄ O ₇	201.43	100.72	0.10072
Sodium Tetraborate (Hydrated)	Na ₂ B ₄ O ₇ · 10H ₂ O	381.43	190.72	0.19072

NORMAL SOLUTIONS OF OXIDIZING AND REDUCING
AGENTS

Compound	Formula	Molecular Weight	Normal Solution Contains gm/l	Milli-Equiv- alent gm/cc
Ammonium Oxalate	$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	142.09	71.05	0.07105
Arsenious Acid	H_3AsO_3	125.93	62.97	0.06297
Arsenious Oxide	As_2O_3	197.82	49.46	0.04946
Bromine	Br	79.916	79.916	0.07992
Calcium Hypochlorite	$\text{Ca}(\text{OCl})_2$	126.99	63.50	0.06350
Chlorine	Cl	35.457	35.457	0.03546
Ferrous Sulphate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278.02	278.02	0.27802
Ferrous Ammonium Sulphate	$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	392.14	392.14	0.39214
Hydrogen Peroxide	H_2O_2	34.02	17.01	0.01701
Hydrogen Sulphide	H_2S	34.08	17.04	0.01704
Iodine	I	126.92	126.92	0.12692
Oxalic Acid	$\text{H}_2\text{C}_2\text{O}_4$	90.036	45.018	0.04502
Oxalic Acid (Hydrated)	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	126.05	63.03	0.06303
Potassium Bromate	KBrO_3	167.02	27.84	0.02784
Potassium Dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$	294.21	49.04	0.04904
Potassium Iodate	KIO_3	214.03	35.67	0.03567
Potassium Permanganate	KMnO_4	158.03	31.61	0.03161
Sodium Thiosulphate	$\text{Na}_2\text{S}_2\text{O}_3$	158.11	158.11	0.15811
Sodium Thiosulphate (Hydrated)	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	248.19	248.19	0.24819
Sodium Oxalate	$\text{Na}_2\text{C}_2\text{O}_4$	133.99	66.995	0.067
Stannous Chloride	SnCl_2	189.61	94.80	0.0948
Stannous Chloride (Hydrated)	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	225.65	112.83	0.11283

NORMAL SOLUTIONS OF PRECIPITATING AGENTS

Compound	Formula	Molecular Weight	Normal Solution Contains gm/l	Milli-Equivalent gm/cc
Ammonium Thiocyanate	NH ₄ SCN	76.11	76.11	0.07611
Hydrochloric Acid	HCl	36.46	36.46	0.03646
Potassium Ferrocyanide	K ₄ Fe(CN) ₆	368.26	368.26	0.36826
Potassium Ferrocyanide (hydrated)	K ₄ Fe(CN) ₆ · 3H ₂ O	422.33	422.33	0.42233
Potassium Thiocyanate	KSCN	97.17	97.17	0.09717
Silver Nitrate	AgNO ₃	169.89	169.89	0.16989
Sodium Chloride	NaCl	58.45	58.45	0.05845

PRIMARY STANDARDS

ACID-BASE

The weights of primary standards in the following tables are based on a titration of 40 cc of 0.1 *N* solution.

Compound	Standard for	Molecular Weight	Milli-Equivalent	Wt. in gm for <i>N</i> /10 Solutions
Guanidine Carbonate	Acid	180.18	0.09009	0.3604
Potassium Bicarbonate	Acid	100.11	0.10011	0.4004
Silver Chloride	HCl	143.34	0.14334	*.
Sodium Carbonate	Acid	106.00	0.05300	0.2120
Sodium Tetraborate	Acid	201.43	0.10072	0.4029
Sodium Tetraborate (decahydrate)	Acid	381.43	0.19072	0.7629
Thallous Carbonate	Acid	468.79	0.23440	0.9376
Adipic Acid	Bases	146.14	0.07307	0.2923
Ammonium Acid Sulphate		115.11	0.11511	0.4604
Ammonium Triiodate		544.82	0.27241	1.0896
Benzoic Acid		122.12	0.12212	0.4885
Boric Acid		61.84	0.02061	0.0824
Mercuric Oxide		232.61	0.11630	0.4652
Oxalic Acid		126.05	0.05303	0.2121
Potassium Acid Phthalate		204.06	0.20406	0.8162
Potassium Biodate		389.85	0.38985	1.5594
Salicylic Acid		138.12	0.06906	0.2762
Sodium Acid Phthalate		189.13	0.18913	0.7565
Succinic Acid		118.09	0.05905	0.2362
Sulfamic Acid		97.49	0.09749	0.3900

* Excess AgNO₃ solution.

OXIDATION-REDUCTION

Compound	Standard for	Moelcular Weight	Milli-Equivalent	Wt. in gm for N/10 Solutions
Ammonium Oxalate (monohydrate)	Permanganate Ceric Sulphate	142.09	0.07106	0.2842
Aniline	Potassium Bromate	93.12	0.01552	0.0621
Arsenious Oxide	Iodine Permanganate Ceric Sulphate	197.82	0.04946	0.1978
Calcium Oxalate	Permanganate Ceric Sulphate	128.08	0.06404	0.2562
Copper	Thiosulphate	63.57	0.06357	0.2543
Copper Oxide	Thiosulphate	79.57	0.07957	0.3183
Copper Sulphate	Thiosulphate Titanous Chloride Titanous Sulphate	160.63	0.16063	0.6425
Ferrous Ammonium Sulphate	Dichromate Permanganate	391.90	0.39190	1.5676
Ferrous Sulphate (heptahydrate)	Permanganate Dichromate	278.01	0.27801	1.1120
Hydrazine Sulphate	Iodine	130.12	0.03251	0.1300
Iodine	Arsenious Acid Thiosulphate	126.96	0.12692	0.5077
Iron	Permanganate	55.84	0.05584	0.2234
Oxalic Acid (dihydrate)	Permanganate	126.05	0.06303	0.2521
Potassium Biiodate	Thiosulphate	389.95	0.03249	0.1300
Potassium Bromate	Thiosulphate	167.02	0.02784	0.1114
Potassium Dichromate	Thiosulphate Titanous Chloride Titanous Sulphate Ferrous Ammonium Sulphate Ferrous Sulphate	291.21	0.04904	0.1962
Potassium Ferricyanide	Titanous Solutions	329.19	0.32919	1.3168

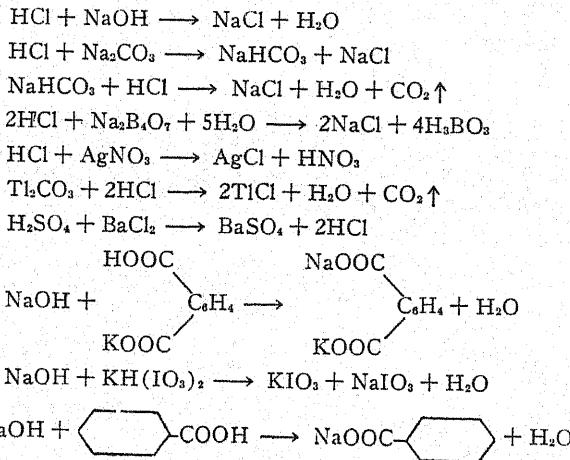
Compound	Standard for	Molecular Weight	Milli-Equivalent	Wt. in gm for N/10 Solutions
Potassium Ferrocyanide (trihydrate)	Permanganate	422.33	0.42233	1.6893
Potassium Iodate	Thiosulphate	214.03	0.03567	0.1427
Potassium Iodide	Thiosulphate	166.02	0.08301	0.3320
	Permanganate			
	Ceric Sulphate			
Potassium Oxalate (monohydrate)	Permanganate	184.22	0.09211	0.3684
	Ceric Sulphate			
Potassium Permanganate	Ferrous Ammonium Sulphate	158.03	0.03161	0.1264
	Ferrous Sulphate			
Silver Nitrate	Iodine	169.89	0.16989	0.6796
Sodium Bromate	Thiosulphate	150.91	0.02515	0.1006
Sodium Iodate	Thiosulphate	197.92	0.03299	0.1320
Sodium Oxalate	Permanganate	133.99	0.0670	0.2680
	Ceric Sulphate			
Sodium Thiosulphate (pentahydrate)	Iodine	248.19	0.24819	0.9928
	Bromate			
Thallous Carbonate	Iodate			
	Iodate	468.78	0.1172	0.4688

PRECIPITATION

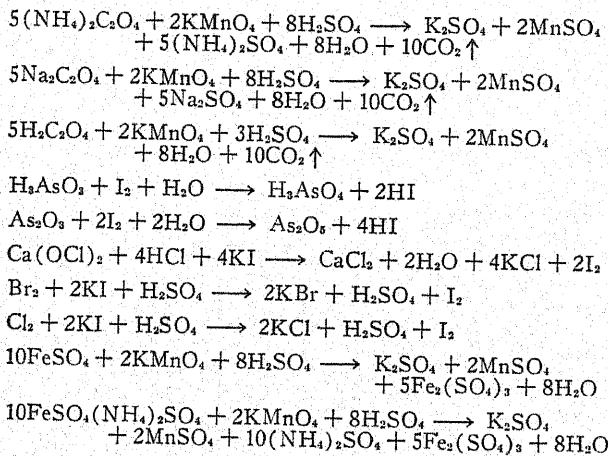
Compound	Standard for	Molecular Weight	Milli-Equivalent	Wt. in gm for N/10 Solutions
Ammonium Thiocyanate	Silver Nitrate	76.11	0.07611	0.3044
Potassium Thiocyanate	Silver Nitrate	97.17	0.09717	0.3887
Silver Nitrate	Thiocyanate	169.89	0.16989	0.6796
Sodium Chloride	Silver Nitrate	58.45	0.05845	0.2338
Zinc Oxide	Potassium Ferrocyanide	422.33	0.21117	0.8447

EQUATIONS INVOLVED IN STANDARDIZATION

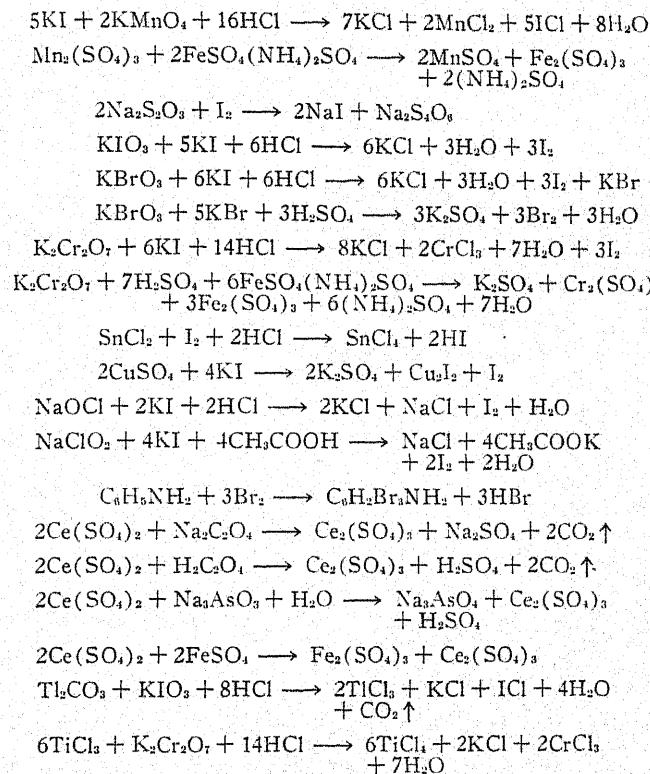
ACID-BASE



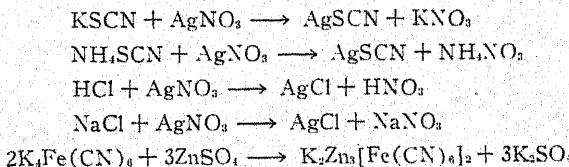
OXIDATION-REDUCTION



OXIDATION-REDUCTION



PRECIPITATION



LOGARITHMS OF VOLUMETRIC FACTORS
BASED ON THE VALUE OF A
NORMAL SOLUTION

ACID-BASE

Compound	Formula	Milli-Equiv- alent	Loga- rithm
Ammonium Hydroxide	NH ₄ OH	0.03505	2.54469
Barium Hydroxide	Ba(OH) ₂	0.08569	2.93293
Hydrochloric Acid	HCl	0.036465	2.56189
Potassium Acid Phthalate	KHO ₄ C ₆ H ₅	0.20406	1.30976
Potassium Iodide	KH(IO ₃) ₂	0.3899	1.59095
Potassium Hydroxide	KOH	0.05610	2.74896
Silver Chloride	AgCl	0.14334	1.15637
Sodium Tetraborate	Na ₂ B ₄ O ₇	0.10072	1.00312
Sodium Tetraborate (Hydrated)	Na ₂ B ₄ O ₇ · 10H ₂ O	0.19072	1.28040
Sodium Carbonate	Na ₂ CO ₃	0.0530	2.72428
Sodium Hydroxide	NaOH	0.0400	2.60206
Sulphuric Acid	H ₂ SO ₄	0.04904	2.69055

LOGARITHMS OF VOLUMETRIC FACTORS
BASED ON THE VALUE OF A
NORMAL SOLUTION

OXIDATION-REDUCTION

Compound	Formula	Milli-Equiv- alent	Loga- rithm
Arsenious Acid	As ₃ O ₃	0.04946	2.69425
Calcium Hypochlorite	Ca (OCl) ₂	0.06350	2.80277
Ceric Sulphate	Ce (SO ₄) ₂	0.33225	1.52147
Chloramine T	p-C ₆ H ₄ CH ₃ SO ₂ N _{Na} Cl	0.14075	1.14845
Copper	Cu	0.06357	2.80325
Copper Sulphate	CuSO ₄	0.15963	1.20311
Ferrous Ammonium Sulphate (Mohr's Salt)	FeSO ₄ · (NH ₄) ₂ - SO ₄ · 6H ₂ O	0.39190	1.59318
Ferrous Sulphate	FeSO ₄ · 7H ₂ O	0.27801	1.44406
Iodine	I	0.12692	1.10353
Oxalic Acid	H ₂ C ₂ O ₄ · 2H ₂ O	0.06303	2.79955
Potassium Bromate	KBrO ₃	0.02784	2.44467
Potassium Dichromate	K ₂ Cr ₂ O ₇	0.04904	2.69055
Potassium Iodate	KIO ₃	0.03567	2.55230
Potassium Permanganate	KMnO ₄	0.03161	2.49982
Sodium Hypochlorite	NaOCl	0.037227	2.57086
Sodium Oxalate	Na ₂ C ₂ O ₄	0.066995	2.82604
Sodium Thiosulphate	Na ₂ S ₂ O ₃	0.15811	1.19896
Sodium Thiosulphate (Hydrated)	Na ₂ S ₂ O ₃ · 5H ₂ O	0.24819	1.39478
Titanium Chloride	TiCl ₄	0.15427	1.18828
Titanium Sulphate	Ti ₂ (SO ₄) ₃	0.38398	1.58431

PRECIPITATION

Compound	Formula	Milli-Equivalent	Logarithm
Ammonium Thiocyanate	NH_4SCN	0.07611	2.88144
Potassium Ferrocyanide	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	0.21117	1.32463
Potassium Thiocyanate	KSCN	0.09717	2.98753
Silver Nitrate	AgNO_3	0.16989	1.23017
Sodium Chloride	NaCl	0.05845	2.76678

ABSOLUTE DENSITY OF WATER *

This table gives the weight in grams of a cubic centimeter of water at temperatures from 0° to 30°C. Water attains its maximum density at 3.98°C., at which temperature the density is 0.999973 (C. G. S.)

Temp. °C.	Density						
0.0	0.999841	7.6	0.999872	15.2	0.999069	22.8	0.997585
0.2	0.9954	7.8	0.9861	15.4	0.9038	23.0	7538
0.4	0.9866	8.0	0.9849	15.6	0.9007	23.2	7490
0.6	0.9878	8.2	0.9837	15.8	0.8975	23.4	7442
0.8	0.9889	8.4	0.9824	16.0	0.8943	23.6	7394
1.0	0.9900	8.6	0.9810	16.2	0.8910	23.8	7345
1.2	0.9903	8.8	0.9785	16.4	0.8877	24.0	7296
1.4	0.9918	9.0	0.9781	16.6	0.8843	24.2	7246
1.6	0.9927	9.2	0.9766	16.8	0.8809	24.4	7198
1.8	0.9934	9.4	0.9751	17.0	0.8774	24.6	7146
2.0	0.9941	9.6	0.9734	17.2	0.8739	24.8	7095
2.2	0.9947	9.8	0.9717	17.4	0.8704	25.0	7044
2.4	0.9953	10.0	0.9700	17.6	0.8668	25.2	6992
2.6	0.9958	10.2	0.9682	17.8	0.8632	25.4	6941
2.8	0.9962	10.4	0.9664	18.0	0.8595	25.6	6888
3.0	0.9965	10.6	0.9645	18.2	0.8558	25.8	6836
3.2	0.9968	10.8	0.9625	18.4	0.8520	26.0	6783
3.4	0.9970	11.0	0.9605	18.6	0.8482	26.2	6729
3.6	0.9972	11.2	0.9585	18.8	0.8444	26.4	6676
3.8	0.9973	11.4	0.9564	19.0	0.8405	26.6	6621
4.0	0.9973	11.6	0.9542	19.2	0.8365	26.8	6567
4.2	0.9973	11.8	0.9520	19.4	0.8325	27.0	6512
4.4	0.9972	12.0	0.9498	19.6	0.8285	27.2	6457
4.6	0.9970	12.2	0.9479	19.8	0.8244	27.4	6401
4.8	0.9968	12.4	0.9451	20.0	0.8203	27.6	6345
5.0	0.9965	12.6	0.9427	20.2	0.8162	27.8	6289
5.2	0.9961	12.8	0.9402	20.4	0.8120	28.0	6232
5.4	0.9957	13.0	0.9377	20.6	0.8078	28.2	6175
5.6	0.9952	13.2	0.9352	20.8	0.8035	28.4	6118
5.8	0.9947	13.4	0.9326	21.0	0.7992	28.6	6060
6.0	0.9941	13.6	0.9299	21.2	0.7948	28.8	6002
6.2	0.9935	13.8	0.9272	21.4	0.7904	29.0	5944
6.4	0.9927	14.0	0.9244	21.6	0.7860	29.2	5885
6.6	0.9920	14.2	0.9216	21.8	0.7815	29.4	5828
6.8	0.9911	14.4	0.9188	22.0	0.7770	29.6	5768
7.0	0.9902	14.6	0.9159	22.2	0.7724	29.8	5706
7.2	0.9893	14.8	0.9129	22.4	0.7678	30.0	5646
7.4	0.9883	15.0	0.9099	22.6	0.7632		

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HYDRATION TEMPERATURES, MELTING
POINTS, AND BOILING POINTS FOR
CALIBRATION OF THERMOMETERS

Compound	Formula	Hydration Temperature
Sodium Chromate	$\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$	19.71 ° C
Sodium Sulphate	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	32.383
Sodium Carbonate	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$	35.3
Sodium Thiosulphate	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	48.0
Sodium Bromide	$\text{NaBr} \cdot 2\text{H}_2\text{O}$	50.8
Manganese Chloride	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	57.8
Trisodium Phosphate	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	73.4
Barium Hydroxide	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	78.0

		Melting Points
Naphthalene	C_{10}H_8	80.8 ° C
Phenanthrene	$(\text{C}_6\text{H}_4\text{CH})_2$	101.0
Benzoic Acid	$\text{C}_6\text{H}_5\text{COOH}$	122.45
Salicylic Acid	$\text{HO} \cdot \text{C}_6\text{H}_4\text{COOH}$	159.8
Anisic Acid	$\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$	184.2
Anthracene	$(\text{C}_6\text{H}_4\text{CH})_2$	216.1
Carbazole	$\text{C}_6\text{H}_5\text{NH} \cdot \text{C}_6\text{H}_4$	247.0
Anthraquinone	$(\text{C}_6\text{H}_4)_2(\text{CO})_2$	285.0

		Boiling Points @ 760 mm
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	110.5 ° C
Monochlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	132.1
Monobromobenzene	$\text{C}_6\text{H}_5\text{Br}$	156.2

REFERENCES

J. Phys. Chem. 6, 85 (1902).
 P. W. Richards and A. H. Fiske, *J. Am. Chem. Soc.* 36, 485 (1914).
 H. C. Dickinson and E. F. Mueller, *J. Am. Chem. Soc.* 29, 1381 (1907).

LOGARITHMS OF NUMBERS

100 — 150

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
100	00 000	043	087	130	173	217	260	303	346	389	432	4.4 43 42
101	432	475	518	561	604	647	689	732	775	817	859	11 4.4 4.3 4.2
102	860	903	945	988	*100	*102	*105	*107	*110	*122	21 8.8 8.6 8.4	
103	01 284	326	368	410	452	494	536	578	620	662	704	31 13.2 12.9 12.6
104	703	745	787	828	870	912	953	995	*036	*078	41 17.6 17.2 16.8	
105	02 119	160	202	243	284	325	366	407	449	490	532	21.5 21.0
106	531	572	612	653	694	727	768	816	857	898	939	6 26.4 25.5 25.2
107	938	978	*019	*060	*100	*141	*181	*222	*262	*302	7 30.8 30.1 29.4	
108	03 342	383	423	463	503	543	583	623	663	703	8 35.2 34.4 33.6	
109	743	782	822	862	902	941	981	*021	*060	*100	9 39.6 38.7 37.8	
110	04 139	179	218	258	297	336	376	415	454	493	531	41 40 39
111	532	571	610	650	689	727	765	805	844	883	921	1 4.1 4.0 3.9
112	922	961	999	*038	*077	*115	*154	*192	*231	*269	2 8.2 8.0 7.8	
113	05 308	346	385	423	461	500	538	576	614	652	691	3 12.3 12.0 11.7
114	690	729	767	805	843	881	918	956	994	*032	4 16.4 16.0 15.6	
115	06 070	108	145	183	221	258	296	333	371	408	510	5 20.5 20.0 19.5
116	446	483	521	558	595	633	670	707	744	781	819	12 4.6 24.0 23.4
117	819	856	893	930	967	*004	*041	*078	*115	*151	7 28.7 28.0 27.3	
118	07 188	225	262	298	335	372	408	445	482	518	556	8 32.8 32.0 31.2
119	655	691	728	764	800	837	873	909	846	882	9 36.9 36.0 35.1	
120	918	954	990	*027	*063	*099	*135	*171	*207	*243	1 11.4 11.1 10.8	
121	08 279	314	350	386	422	458	493	529	565	600	638	3 37 36
122	636	672	707	743	778	814	849	884	920	955	7 21.6 22.2 21.6	
123	991	*026	*061	*096	*132	*167	*202	*237	*272	*307	2 7.6 7.4 7.2	
124	09 342	377	412	447	482	517	552	587	621	656	694	4 15.2 14.8 14.4
125	691	726	760	795	830	864	899	934	968	*003	5 14.2 13.3 12.4	
126	10 037	072	106	140	175	209	243	278	312	346	381	19.0 18.5 18.0
127	380	415	449	483	517	551	585	619	653	687	724	6 22.8 22.2 21.6
128	721	755	789	823	857	890	924	958	992	*025	7 24.6 25.2 25.2	
129	11 059	093	126	160	193	227	261	294	327	361	396	29.6 31.8 31.8
130	394	428	461	494	528	561	594	628	661	694	731	35 34 33
131	727	760	793	826	860	893	926	959	992	*024	11 3.5 3.4 3.3	
132	12 057	090	123	155	189	222	254	287	320	352	387	2 7.0 6.8 6.6
133	385	418	450	483	516	548	581	613	646	678	710	310.5 10.2 9.9
134	710	743	775	808	840	872	905	937	969	*001	4 14.0 13.6 13.2	
135	13 033	066	098	130	162	194	226	258	290	322	359	517.5 17.4 16.5
136	354	388	418	450	481	513	545	577	609	640	677	6 21.0 20.4 19.8
137	672	704	735	767	799	830	862	893	925	956	7 24.5 23.8 23.1	
138	988	*019	*051	*082	*114	*145	*176	*208	*239	*270	8 28.0 27.2 26.4	
139	14 301	333	364	395	426	457	489	520	551	582	619	9 31.5 30.6 29.7
140	613	644	675	706	737	768	799	829	860	891	920	4 12.8 12.4 12.0
141	922	953	983	*014	*045	*076	*105	*137	*168	*198	32	31 30
142	15 229	259	290	320	351	381	412	442	473	503	534	1 3.2 3.1 3.0
143	534	564	594	625	655	685	715	746	776	806	836	2 6.4 6.2 6.0
144	836	866	897	927	957	987	*017	*047	*077	*107	3 9.6 9.3 9.0	
145	16 137	167	197	227	256	286	316	346	376	406	436	5 16.0 15.5 15.0
146	435	465	495	524	554	584	613	643	673	702	732	6 19.2 18.6 18.0
147	732	761	791	820	850	875	905	938	967	997	1027	7 22.4 21.7 21.0
148	17 026	056	085	114	143	173	202	231	260	289	318	8 25.6 24.8 24.0
149	319	348	377	406	435	464	493	522	551	580	609	9 28.8 27.9 27.0
150	609	638	667	696	725	754	782	811	840	869	-	Proportional parts
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

.00000 — .17869

LOGARITHMS OF NUMBERS

150 — 200

N.	L	0	1	2	3	4	5	6	7	8	9	Proportional parts	
150	17	609	638	667	696	725	754	782	811	840	869	29 28	
151	898	926	955	984	*013	*041	*070	*099	*127	*156	1	14.5 2.8	
152	18	104	213	241	270	298	327	355	384	412	441	2 5.8 5.4	
153	469	498	526	554	583	611	639	667	696	724	753	3 8.7 8.4	
154	752	780	808	837	865	893	921	949	977	*005	4	11.6 11.2	
155	19	033	061	089	117	145	173	201	229	257	285	5 14.5 14.0	
156	312	340	368	396	424	451	479	507	535	562	590	6 17.4 16.8	
157	590	618	645	673	700	728	756	783	811	838	865	7 20.3 19.6	
158	866	893	921	948	976	*003	*030	*058	*085	*112	1	23.2 22.4	
159	20	140	167	194	222	249	276	303	330	358	385	9 26.1 25.4	
160	412	439	466	493	520	548	575	602	629	656	683	27 26	
161	683	710	737	763	790	817	844	871	898	925	952	1 2.7 2.6	
162	952	978	*005	*032	*059	*085	*112	*139	*165	*192	2	5.4 5.2	
163	21	219	245	272	299	325	352	378	405	431	458	3 7.4	
164	484	511	537	564	590	617	643	669	696	722	749	4 10.3 10.4	
165	748	775	801	827	854	880	906	932	958	985	1012	5 13.5 13.0	
166	22	011	037	063	089	115	141	167	194	220	246	6 16.2 15.6	
167	272	298	324	350	376	401	427	453	479	505	531	7 18.9 18.2	
168	531	557	583	608	634	660	686	712	737	763	789	8 21.6 20.8	
169	789	814	840	866	891	917	943	968	994	*019	9	24.3 23.4	
170	23	045	070	096	121	147	172	198	223	249	274	25	
171	300	325	350	376	401	426	452	477	502	528	554	1 2.5	
172	553	578	603	629	654	679	704	729	754	779	804	2 5.0	
173	808	830	855	880	905	930	955	980	*005	*030	3	7.5	
174	24	055	080	105	130	155	180	204	229	254	279	4 10.0	
175	304	329	353	378	403	428	452	477	502	527	552	5 12.5	
176	551	576	601	625	650	674	699	724	749	773	800	6 15.0	
177	797	822	846	871	895	920	944	969	993	*018	10	7 17.5	
178	25	042	066	091	115	139	164	188	212	237	261	8 20.0	
179	285	310	334	358	382	406	431	455	479	503	528	9 22.5	
180	527	551	575	600	624	648	672	696	720	744	768	24 23	
181	768	792	816	840	864	888	912	935	959	983	1007	1 2.4 2.3	
182	26	007	031	055	079	102	126	150	174	198	221	2	4.8 4.6
183	245	269	293	316	340	364	387	411	435	458	481	3 7.2	
184	482	505	529	553	576	600	623	647	670	694	717	4 9.6	
185	717	741	764	788	811	834	858	881	905	928	951	5 12.5 11.5	
186	951	975	998	*021	*045	*068	*091	*114	*138	*161	1	14.4 13.8	
187	27	184	207	231	254	277	300	323	346	370	393	4 15.8 15.1	
188	416	439	462	485	508	531	554	577	600	623	646	7 18.8 18.1	
189	646	669	692	715	738	761	784	807	830	852	875	8 20.2	
190	875	898	921	944	967	989	*012	*035	*058	*081	9	21.6 20.7	
191	28	103	126	149	171	194	217	240	262	285	307	22 21	
192	330	353	375	398	421	443	466	488	511	533	555	1 2.2	
193	568	578	601	625	646	668	691	713	735	758	780	2 4.4	
194	780	803	825	847	870	892	914	937	959	981	1003	3 6.6	
195	29	003	026	048	070	092	115	137	159	181	203	4 8.8	
196	226	248	270	292	314	336	358	380	403	425	447	5 11.0	
197	447	469	491	513	535	557	579	601	623	645	667	6 13.2	
198	667	688	710	732	754	776	798	820	842	863	885	7 15.4	
199	885	907	929	951	973	994	*016	*038	*060	*081	1	17.6	
200	30	103	125	146	168	190	211	233	255	276	298	9 19.8	

.17 609 — .30 298

LOGARITHMS OF NUMBERS

200 — 250

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts	
200	30	103	125	146	168	190	211	233	255	276	298	22 21	
201	320	341	363	384	406	428	449	471	492	514	1 2.2	2.1	
202	535	557	578	600	621	643	664	685	707	728	2 4.4	4.2	
203	750	771	792	814	835	856	878	899	920	942	3 6.6	6.3	
204	963	984	*006	*027	*049	*069	*091	*112	*133	*154	4 8.8	8.4	
205	31	175	197	218	239	260	281	302	323	345	366	5 11.0	10.5
206	337	408	429	450	471	492	513	534	555	576	597	6 13.2	12.6
207	597	618	639	660	681	702	723	744	765	785	805	7 15.4	14.7
208	808	827	848	869	890	911	931	952	973	994	1015	8 17.6	16.8
209	32 015	035	056	077	098	118	139	160	181	201	9 19.8	18.9	
210	222	243	263	284	305	325	346	366	387	408	429	20	
211	428	449	469	490	510	531	552	572	593	613	633	1 2.5	
212	634	654	675	695	715	736	756	777	797	818	838	2 4.0	
213	838	858	879	899	919	940	960	980	*001	*021	203	3 6.0	
214	33 041	062	082	102	122	143	163	183	203	224	244	4 8.0	
215	244	264	284	304	325	345	365	385	405	425	445	5 10.0	
216	445	465	485	505	526	546	566	586	606	626	646	6 12.0	
217	646	666	686	706	726	746	766	786	806	826	846	7 14.0	
218	846	866	885	905	925	945	965	985	*005	*025	203	8 16.0	
219	34 044	054	084	104	124	143	163	183	203	223	243	9 18.0	
220	242	262	282	301	321	341	361	380	400	420	440	19	
221	439	459	479	498	518	537	557	577	596	616	636	1 1.9	
222	635	655	674	694	713	733	753	772	792	811	831	2 3.9	
223	830	850	869	889	908	928	947	967	986	*005	203	3 5.7	
224	35 025	044	064	083	102	122	141	160	180	199	219	4 7.6	
225	218	238	257	276	295	315	334	353	372	392	412	5 9.5	
226	411	430	449	468	488	507	526	545	564	583	603	6 11.4	
227	603	622	641	660	679	698	717	736	755	774	794	7 13.3	
228	793	813	832	851	870	889	908	927	946	965	985	8 15.2	
229	984	*003	*021	*040	*059	*078	*097	*116	*135	*154	203	9 17.1	
230	36 173	192	211	229	248	267	286	305	324	342	362	18	
231	361	380	399	418	436	455	474	493	511	530	549	1 1.8	
232	549	568	586	605	624	642	661	680	698	717	736	2 3.6	
233	736	754	773	791	810	*829	*847	*866	*884	*903	*923	3 5.4	
234	922	940	959	977	996	*014	*033	*051	*070	*088	*107	4 7.2	
235	37 107	125	144	162	181	199	218	236	254	273	292	5 9.0	
236	291	310	328	346	365	383	401	420	438	457	476	6 10.8	
237	475	493	511	530	548	566	585	603	621	639	658	7 12.6	
238	658	676	694	712	731	749	767	785	803	822	841	8 14.4	
239	840	858	876	894	912	931	949	967	985	*003	203	9 16.2	
240	38 021	039	057	075	093	112	130	148	166	184	202	17	
241	202	220	238	256	274	292	310	328	346	364	382	1 1.7	
242	382	399	417	435	453	471	489	507	525	543	561	2 3.4	
243	561	578	596	614	632	650	668	686	703	721	739	3 5.1	
244	739	757	775	792	810	828	846	863	881	899	203	4 6.8	
245	917	934	952	970	987	*005	*023	*041	*058	*076	203	5 8.5	
246	38 094	111	129	146	164	182	199	217	235	252	270	6 10.2	
247	270	287	305	322	340	358	375	393	410	428	446	7 11.9	
248	445	463	480	498	515	533	550	568	585	602	620	8 13.6	
249	620	637	655	672	690	707	724	742	759	777	203	9 15.3	
250	794	811	829	846	863	881	898	915	933	950	203	Proportional parts	
N.	L.	0	1	2	3	4	5	6	7	8	9		

.30 103 — .59 950

LOGARITHMS OF NUMBERS

250 — 300

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts	
250	39	794	811	829	846	862	881	898	915	933	950	18	
251	967	985	*002	*019	*037	*054	*071	*088	*106	*123		1.6	
252	40	140	157	175	192	209	226	243	261	278	295	2	
253	312	329	346	364	381	398	415	432	450	468		5.6	
254	483	500	518	535	552	569	586	603	620	637		5.4	
255	654	671	688	705	722	739	756	773	790	807		7.2	
256	824	841	858	875	892	909	926	943	960	976		9.0	
257	993	*010	*027	*044	*061	*078	*095	*111	*128	*145		10.8	
258	41	162	179	196	212	229	246	263	280	296	313	12.6	
259	330	347	363	380	397	414	430	447	464	481		14.4	
260	497	514	531	547	564	581	597	614	631	647		16	
261	664	681	697	714	731	747	764	780	797	814		1.7	
262	830	847	863	880	896	913	929	946	963	979		3.4	
263	996	*012	*029	*045	*062	*078	*095	*111	*127	*144		5.1	
264	42	160	177	193	210	226	243	259	275	292	308	6.8	
265	325	341	357	374	390	406	423	439	455	472		8.5	
266	488	504	521	537	553	570	586	602	619	635		10.2	
267	651	*667	684	700	716	732	749	765	781	797		11.9	
268	813	830	846	862	878	894	911	927	943	959		13.6	
269	975	*991	*008	*024	*040	*056	*072	*088	*104	*120		15.3	
270	43	136	152	169	185	201	217	233	249	265	281	16	
271	297	313	329	345	361	377	393	409	425	441		1.6	
272	457	473	489	505	521	537	553	569	584	600		3.2	
273	616	632	648	664	680	696	712	727	743	759		4.8	
274	775	791	807	823	838	854	870	886	902	917		6.4	
275	933	949	965	981	996	*012	*028	*044	*059	*075		8.0	
276	44	091	107	122	138	154	170	185	201	217	232	9.6	
277	248	264	279	295	311	326	342	358	373	389		11.2	
278	404	420	436	451	467	483	498	514	529	545		12.8	
279	560	576	592	607	623	638	654	669	685	700		14.4	
280	716	731	747	762	778	793	809	824	840	855		15	
281	871	886	902	917	932	948	963	979	994	*010		1.5	
282	45	025	040	056	071	086	102	117	133	148	163	3.0	
283	179	194	209	225	240	255	271	286	301	317		4.5	
284	332	347	362	378	393	408	423	439	454	469		6.0	
285	484	500	515	530	545	561	576	591	606	621		7.5	
286	637	652	667	682	697	712	728	743	758	773		9.0	
287	788	803	818	834	849	864	879	894	909	924		10.5	
288	939	954	969	984	*000	*015	*030	*045	*060	*075		12.0	
289	46	090	105	120	135	150	165	180	195	210	225	13.5	
290	240	255	270	285	300	315	330	345	359	374		14	
291	389	404	419	434	449	464	479	494	509	523		1.4	
292	538	553	568	583	598	613	627	642	657	672		2.8	
293	687	702	716	731	746	761	776	790	805	820		4.2	
294	835	850	864	879	894	909	923	938	953	967		5.6	
295	982	997	*012	*026	*041	*056	*070	*085	*100	*114		7.0	
296	47	129	144	159	173	188	202	217	232	246	261	8.4	
297	276	290	305	319	334	349	363	378	392	407		9.8	
298	422	436	451	465	480	494	509	524	538	553		11.2	
299	567	582	596	611	626	640	654	669	683	698		12.6	
300	712	727	741	756	770	784	799	813	828	842	log e = 0.43429		
	N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

.39 794 — .47 842

LOGARITHMS OF NUMBERS

300 — 350

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
300	47	712	727	741	756	770	784	799	813	828	842	
301	857	871	885	900	914	929	943	958	972	986		1 1.5
302	48 001	015	029	044	058	073	087	101	116	130		2 3.0
303	144	159	173	187	202	216	230	244	258	273		3 4.5
304	287	302	316	330	344	359	373	387	401	416		4 6.0
305	430	444	458	473	487	501	515	530	544	558		5 7.5
306	572	586	601	615	629	643	657	671	685	700		6 9.0
307	714	728	742	756	770	785	799	813	827	841		7 10.5
308	855	869	883	897	911	926	940	954	968	982		8 12.0
309	996	*010	*024	*038	*052	*066	*080	*094	*108	*122		9 13.5
310	49 136	150	164	178	192	206	220	234	248	262		14
311	276	290	304	318	332	346	360	374	388	402		1 1.4
312	415	429	443	457	471	485	499	513	527	541		2 2.8
313	554	568	582	596	610	624	638	651	665	679		3 4.2
314	693	707	721	734	748	762	776	790	803	817		4 5.6
315	831	845	859	872	886	890	914	927	941	955		5 7.0
316	969	982	996	*010	*024	*037	*051	*065	*079	*092		6 8.4
317	50 106	120	133	147	161	174	188	202	215	229		7 9.8
318	243	256	270	284	297	311	325	338	352	365		8 11.2
319	379	393	406	420	433	447	461	474	488	501		9 12.6
320	515	529	542	556	569	583	596	610	623	637		
321	651	664	678	691	705	718	732	745	759	772		
322	786	799	813	826	840	853	866	880	893	907		
323	920	934	947	961	974	987	*001	*014	*028	*041		
324	51 055	068	081	095	108	121	135	148	162	175		
325	188	202	215	228	242	255	268	282	295	308		
326	322	335	348	362	375	388	402	415	428	441		13
327	455	468	481	495	508	521	534	548	561	574		
328	587	601	614	627	640	653	666	680	693	706		1 1.3
329	720	733	746	759	772	785	799	812	825	838		2 2.4
330	851	865	878	891	904	917	930	943	957	970		3 3.9
331	983	996	*009	*022	*035	*048	*061	*075	*088	*101		4 5.2
332	52 114	127	140	153	166	179	192	205	218	231		5 6.5
333	244	257	270	284	297	310	323	336	349	362		6 7.8
334	375	388	401	414	427	440	453	466	479	492		7 9.1
335	604	517	530	543	556	569	582	595	608	621		8 10.4
336	634	647	660	673	685	699	711	724	737	750		9 11.7
337	763	776	789	802	815	827	840	853	866	879		
338	892	905	917	930	943	956	969	982	994	*007		
339	53 020	033	046	058	071	084	097	110	122	135		12
340	148	161	173	186	199	212	224	237	250	263		1 1.3
341	275	288	301	314	326	339	352	364	377	390		2 2.4
342	403	415	428	441	453	466	479	491	504	517		3 3.6
343	529	542	555	567	580	593	605	618	631	643		4 4.8
344	656	668	681	694	706	719	732	744	757	769		5 6.0
345	782	794	807	820	832	845	857	870	882	895		6 7.2
346	908	920	933	945	958	970	983	995	*008	*020		7 8.4
347	54 033	045	058	070	083	095	108	120	133	145		8 9.6
348	158	171	183	195	208	220	233	245	258	270		9 10.8
349	283	295	307	320	332	345	357	370	382	394		
350	407	419	432	444	456	469	481	494	506	518	log π = 0.49715	
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

47 712 -- .54 518

LOGARITHMS OF NUMBERS

350 — 400

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
350	54	407	419	432	444	456	469	481	494	506	518	
351	531	513	555	568	580	593	605	617	630	642		
352	654	667	679	691	704	716	728	741	753	765		
353	777	790	802	814	827	839	851	864	876	888		
354	900	913	925	937	949	962	974	986	998	*011		
355	55	023	035	047	060	072	084	096	108	121	133	
356	145	157	169	182	194	206	218	230	242	255		1 1.3
357	267	279	291	303	315	328	340	352	364	376		2 2.6
358	388	400	413	425	437	449	461	473	485	497		3 3.9
359	509	522	534	546	558	570	582	594	606	618		4 5.2
360	630	642	654	666	678	691	703	715	727	739		5 6.5
361	751	763	775	787	799	811	823	835	847	859		6 7.8
362	871	883	895	907	919	931	943	955	967	979		7 9.1
363	991	*003	*015	*027	*038	*050	*062	*074	*086	*098		8 10.4
364	56	110	122	134	146	158	170	182	194	205	217	9 11.7
365	229	241	253	265	277	289	301	312	324	336		
366	318	330	342	354	366	387	401	413	425	437		1 1.2
367	457	478	490	502	514	526	538	550	561	573		2 2.4
368	585	597	608	620	632	642	655	667	679	691		3 3.6
369	703	714	726	738	750	761	773	785	797	808		4 4.8
370	820	832	844	855	867	879	891	902	914	926		5 6.0
371	937	949	961	972	984	996	*008	*019	*031	*043		6 7.2
372	57	054	066	078	089	101	113	124	136	148	159	7 8.4
373	171	183	194	206	217	229	241	252	264	276		8 9.6
374	287	299	310	322	334	345	357	368	380	392		9 10.8
375	403	415	426	438	449	461	473	484	496	507		
376	519	530	542	553	565	576	588	600	612	623		1 1.1
377	634	646	657	669	680	692	703	715	726	738		2 2.2
378	749	761	772	784	795	807	818	830	841	852		3 3.3
379	864	875	887	898	910	921	933	944	955	967		4 4.4
380	978	990	*001	*013	*024	*035	*047	*058	*070	*081		5 5.5
381	58	092	104	115	127	138	149	161	172	184	195	
382	206	218	229	240	252	263	274	286	297	309		6 6.6
383	320	331	343	354	365	377	388	399	410	422		7 7.7
384	433	444	456	467	478	490	501	512	524	535		8 8.8
385	546	557	569	580	591	602	614	625	636	647		9 9.9
386	659	670	681	692	704	715	726	737	749	760		
387	771	782	794	806	818	827	838	850	861	872		
388	883	894	906	917	928	939	950	961	973	984		
389	995	*006	*017	*028	*040	*051	*062	*073	*084	*095		
390	59	106	118	129	140	151	162	173	184	195	207	
391	218	229	240	251	262	273	284	295	306	318		1 1.0
392	329	340	351	362	373	384	395	406	417	428		2 2.0
393	439	450	461	472	483	494	506	517	528	539		3 3.0
394	550	561	572	583	594	605	616	627	638	649		4 4.0
395	660	671	682	693	704	715	726	737	748	759		5 5.0
396	770	780	791	802	813	823	834	845	857	868		6 6.0
397	873	880	891	901	912	923	934	945	956	967		7 7.0
398	988	995	*010	*021	*032	*043	*054	*065	*076	*087		8 8.0
399	60	097	108	119	130	141	152	163	173	184	195	9 9.0
400	206	217	228	239	249	260	271	282	293	304		
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

.54 407 — .60 304

LOGARITHMS OF NUMBERS

400 — 450

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
400	60	5106	217	228	239	249	260	271	282	293	304	
401	61	5126	215	236	347	358	369	379	390	401	412	
402	62	5143	433	444	507	513	466	477	487	498	509	520
403	63	5151	433	444	507	513	466	477	487	498	509	520
404	64	5158	649	660	670	681	692	703	713	724	735	
405	746	756	767	778	789	799	810	821	831	842		
406	853	863	874	885	895	905	917	927	937	947	959	11
407	959	970	981	991	*002	*013	*023	*034	*045	*056		
408	61	666	077	087	108	119	130	140	151	162	173	1
409	172	183	194	204	215	225	236	247	257	268	279	2
410	410	395	389	380	370	361	352	342	332	323	313	3
411	412	405	416	426	437	448	458	468	478	488	498	4
412	413	593	606	617	627	637	647	657	667	677	687	5.5
413	700	711	721	721	721	721	721	721	721	721	721	4.4
414	415	805	815	826	836	847	857	867	878	888	898	4.4
415	805	920	930	941	951	962	972	982	992	999		5.5
416	62	014	024	034	045	055	065	076	086	096	099	6.6
417	418	118	128	138	149	159	170	180	190	200	210	7.7
418	419	221	232	242	252	263	273	284	294	304	315	8.8
420	325	335	346	356	366	377	387	397	408	418	428	9.9
421	422	428	439	449	459	469	480	490	500	510	521	1.0
422	523	542	552	562	572	583	593	603	613	624	634	2.2
423	624	644	654	665	675	685	695	705	716	726	736	3.0
424	737	747	757	767	778	788	798	808	818	829	839	4.0
425	839	849	859	870	880	890	900	910	921	931	941	5.0
426	941	951	961	972	982	992	*002	*012	*022	*032	*042	6.0
427	63	043	053	063	073	083	093	103	113	123	133	7.0
428	429	144	155	165	175	185	195	205	215	225	235	8.0
429	246	256	266	276	286	296	306	316	327	337	347	9.0
430	347	357	367	377	387	397	407	417	428	438	448	
431	432	446	456	468	478	488	498	508	518	528	538	
432	546	556	568	578	589	599	609	619	629	639	649	
433	656	666	676	686	696	706	716	726	736	746	756	
434	756	766	776	786	796	806	816	826	836	846	856	
435	849	859	869	879	889	899	909	919	929	939	949	9
436	949	959	969	979	989	999	*009	*019	*029	*039		1.0
437	64	048	058	068	078	088	098	108	118	128	138	2.1
438	147	157	167	177	187	197	207	217	227	237	247	3.2
439	246	256	266	276	286	296	306	316	326	336	346	4.3
440	345	355	365	375	385	395	404	414	424	434	444	5.4
441	442	454	464	473	483	493	503	513	523	532	542	6.5
442	552	562	572	582	592	601	611	621	631	641	651	7.6
443	660	660	670	680	690	699	709	719	729	739	749	8.7
444	758	768	778	788	798	807	817	826	836	846	856	9.8
445	836	846	856	866	875	885	895	904	914	924		
446	933	943	953	963	972	982	992	*002	*011	*021		
447	65	031	040	050	060	070	080	090	100	110		
448	128	137	147	157	167	176	186	196	206	216		
449	225	234	244	254	263	273	283	292	302	312		
450	321	331	341	350	360	369	379	389	398	408		
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

LOGARITHMS OF NUMBERS

450 — 500

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
450	65	321	331	341	350	360	369	379	389	398	408	
451	66	322	332	342	351	361	370	380	390	400	410	1.0
452	67	323	333	343	352	362	371	381	391	401	411	1.0
453	68	324	334	344	353	363	372	382	392	402	412	1.0
454	69	325	335	345	354	364	373	383	393	403	413	1.0
455	70	326	336	346	355	365	374	384	394	404	414	1.0
456	71	327	337	347	356	366	375	385	395	405	415	1.0
457	72	328	338	348	357	367	376	386	396	406	416	1.0
458	73	329	339	349	358	368	377	387	397	407	417	1.0
459	74	330	340	350	360	370	379	389	399	409	419	1.0
460	75	331	341	351	361	371	380	390	400	410	420	1.0
461	76	332	342	352	362	372	381	391	401	411	421	1.0
462	77	333	343	353	363	373	382	392	402	412	422	1.0
463	78	334	344	354	364	374	383	393	403	413	423	1.0
464	79	335	345	355	365	375	384	394	404	414	424	1.0
465	80	336	346	356	366	376	385	395	405	415	425	1.0
466	81	337	347	357	367	377	386	396	406	416	426	1.0
467	82	338	348	358	368	378	387	397	407	417	427	1.0
468	83	339	349	359	369	379	388	398	408	418	428	1.0
469	84	340	350	360	370	380	389	399	409	419	429	1.0
470	85	341	351	361	371	381	390	400	410	420	430	1.0
471	86	342	352	362	372	382	391	401	411	421	431	1.0
472	87	343	353	363	373	383	392	402	412	422	432	1.0
473	88	344	354	364	374	384	393	403	413	423	433	1.0
474	89	345	355	365	375	385	394	404	414	424	434	1.0
475	90	346	356	366	376	386	395	405	415	425	435	1.0
476	91	347	357	367	377	387	396	406	416	426	436	1.0
477	92	348	358	368	378	388	397	407	417	427	437	1.0
478	93	349	359	369	379	389	398	408	418	428	438	1.0
479	94	350	360	370	380	390	399	409	419	429	439	1.0
480	95	351	361	371	381	391	400	410	420	430	440	1.0
481	96	352	362	372	382	392	401	411	421	431	441	1.0
482	97	353	363	373	383	393	402	412	422	432	442	1.0
483	98	354	364	374	384	394	403	413	423	433	443	1.0
484	99	355	365	375	385	395	404	414	424	434	444	1.0
485	100	356	366	376	386	396	405	415	425	435	445	1.0
486	101	357	367	377	387	397	406	416	426	436	446	1.0
487	102	358	368	378	388	398	407	417	427	437	447	1.0
488	103	359	369	379	389	399	408	418	428	438	448	1.0
489	104	360	370	380	390	400	409	419	429	439	449	1.0
490	105	361	371	381	391	401	410	420	430	440	450	1.0
491	106	362	372	382	392	402	411	421	431	441	451	1.0
492	107	363	373	383	393	403	412	422	432	442	452	1.0
493	108	364	374	384	394	404	413	423	433	443	453	1.0
494	109	365	375	385	395	405	414	424	434	444	454	1.0
495	110	366	376	386	396	406	415	425	435	445	455	1.0
496	111	367	377	387	397	407	416	426	436	446	456	1.0
497	112	368	378	388	398	408	417	427	437	447	457	1.0
498	113	369	379	389	399	409	418	428	438	448	458	1.0
499	114	370	380	390	400	410	419	429	439	449	459	1.0
500	115	371	381	391	401	411	420	430	440	450	460	1.0
N.		0	1	2	3	4	5	6	7	8	9	Proportional parts
L.		1	2	3	4	5	6	7	8	9		

LOGARITHMS OF NUMBERS

500 — 550

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
500		500	500	500	500	500	500	500	500	500	500	
501	69	593	596	599	601	603	605	607	609	610	611	*0.027
502	70	597	600	603	605	607	609	611	613	615	616	*0.036
503	157	665	668	671	674	677	680	683	686	689	692	*0.044
504	243	752	756	760	763	767	770	774	778	782	786	*0.053
505	329	838	846	854	862	870	878	886	894	902	910	*0.062
506	415	924	932	941	950	959	968	976	985	994	1002	*0.071
507	501	995	518	526	535	544	553	562	571	580	589	*0.080
508	596	603	612	621	630	639	648	657	666	675	684	*0.089
509	692	680	689	697	706	714	723	731	740	749	758	*0.098
510	787	766	774	783	791	799	808	817	825	834	843	*0.107
511	842	835	844	853	862	871	880	889	898	907	916	*0.116
512	927	935	944	953	962	971	980	989	998	1007	1016	*0.125
513	71	012	020	029	037	045	053	061	069	078	086	*0.003
514	096	105	113	122	130	139	147	156	164	172	180	*0.012
515	181	189	198	206	214	223	231	240	248	257	265	*0.021
516	263	273	282	291	299	307	315	324	332	341	350	*0.030
517	349	357	366	374	383	391	399	408	416	425	434	*0.039
518	435	441	450	458	466	475	483	492	500	508	517	*0.048
519	517	526	533	542	550	559	567	575	584	592	601	*0.057
520	600	609	617	625	634	642	650	659	667	675	683	*0.066
521	694	692	700	708	716	724	732	740	748	756	764	*0.075
522	787	775	784	792	801	809	817	825	834	842	850	*0.084
523	880	888	897	905	913	921	929	937	945	953	961	*0.093
524	933	941	950	958	966	975	983	991	999	1007	1015	*0.102
525	72	016	024	032	040	049	057	066	074	082	090	*0.011
526	099	107	115	123	132	140	148	156	165	173	181	*0.020
527	199	198	206	214	222	230	239	247	255	263	271	*0.029
528	283	272	280	288	296	304	313	321	329	337	345	*0.038
529	346	344	352	360	368	376	384	393	401	409	417	*0.047
530	428	436	444	452	460	468	477	485	493	501	509	*0.056
531	510	518	526	534	542	550	558	567	575	583	591	*0.065
532	591	599	607	615	624	632	640	648	656	664	672	*0.074
533	673	681	689	697	705	713	721	729	736	744	752	*0.083
534	754	762	770	778	787	795	803	811	819	827	835	*0.092
535	835	843	852	860	868	876	884	892	900	908	916	*0.101
536	916	923	930	938	945	953	960	968	975	983	991	*0.110
537	997	*095	933	941	949	957	965	973	981	989	997	*0.119
538	73	078	085	092	099	106	113	120	127	135	143	*0.020
539	159	167	175	183	191	199	207	215	223	231	239	*0.029
540	239	247	255	263	272	280	288	296	304	312	320	*0.038
541	320	328	336	344	352	360	368	376	384	392	400	*0.047
542	400	408	416	424	432	440	448	456	464	472	480	*0.056
543	480	488	496	504	512	520	528	536	544	552	560	*0.065
544	568	576	584	592	600	608	616	624	632	640	648	*0.074
545	640	648	656	664	672	680	688	696	704	712	720	*0.083
546	729	727	735	751	759	767	775	783	791	799	807	*0.092
547	809	807	815	823	831	839	847	855	863	871	879	*0.101
548	886	885	893	902	910	918	926	934	941	949	957	*0.110
549	957	955	963	961	969	977	985	993	1000	1008	1016	*0.119
550	74	035	044	052	060	068	075	084	092	099	107	*0.028
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

Proportional parts

LOGARITHMS OF NUMBERS

550 — 600

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional part
550	74	0.935	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94
551	115	1.115	1.115	1.115	1.115	1.115	1.115	1.115	1.115	1.115	1.115	1.115
552	194	2.02	2.01	2.01	2.01	2.01	2.01	2.01	2.01	2.01	2.01	2.01
553	323	2.80	2.80	2.80	2.80	2.80	2.80	2.80	2.80	2.80	2.80	2.80
554	351	3.09	3.07	3.07	3.07	3.07	3.07	3.07	3.07	3.07	3.07	3.07
555	429	4.13	4.13	4.13	4.13	4.13	4.13	4.13	4.13	4.13	4.13	4.13
556	595	6.03	6.03	6.03	6.03	6.03	6.03	6.03	6.03	6.03	6.03	6.03
557	585	6.93	6.93	6.93	6.93	6.93	6.93	6.93	6.93	6.93	6.93	6.93
558	632	6.71	6.71	6.71	6.71	6.71	6.71	6.71	6.71	6.71	6.71	6.71
559	741	7.9	7.9	7.9	7.9	7.9	7.9	7.9	7.9	7.9	7.9	7.9
560	819	8.27	8.34	8.42	8.50	8.58	8.65	8.73	8.81	8.89	8.97	8.9
561	806	9.04	9.04	9.04	9.04	9.04	9.04	9.04	9.04	9.04	9.04	9.04
562	974	9.81	9.89	9.97	9.97	9.97	9.97	9.97	9.97	9.97	9.97	9.97
563	75	0.51	0.59	0.66	0.74	0.82	0.90	0.98	1.06	1.15	1.23	1.32
564	128	1.36	1.43	1.51	1.59	1.67	1.75	1.83	1.91	1.99	2.07	2.14
565	205	2.13	2.20	2.28	2.36	2.43	2.51	2.59	2.67	2.74	2.82	2.9
566	282	2.95	3.02	3.09	3.16	3.23	3.30	3.37	3.44	3.51	3.58	3.64
567	358	3.95	4.02	4.09	4.16	4.23	4.30	4.37	4.44	4.51	4.58	4.64
568	511	4.42	4.49	4.56	4.63	4.70	4.77	4.84	4.91	4.98	5.04	5.1
569	619	5.26	5.34	5.42	5.50	5.58	5.65	5.73	5.81	5.89	5.97	6.04
570	587	5.95	6.03	6.10	6.18	6.26	6.33	6.41	6.48	6.56	6.63	6.71
571	764	6.71	6.79	6.86	6.94	7.02	7.09	7.17	7.24	7.32	7.4	7.48
572	572	7.47	7.55	7.63	7.71	7.78	7.85	7.93	8.00	8.08	8.16	8.24
573	815	8.51	8.58	8.65	8.72	8.79	8.86	8.93	8.98	9.05	9.12	9.19
574	823	9.21	9.28	9.35	9.42	9.49	9.56	9.63	9.7	9.77	9.84	9.91
575	891	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9
576	975	9.67	9.74	9.81	9.88	9.95	1.02	1.09	1.16	1.23	1.3	1.38
577	573	1.18	1.25	1.33	1.4	1.48	1.55	1.63	1.7	1.78	1.85	1.92
578	193	2.00	2.08	2.16	2.23	2.3	2.38	2.45	2.53	2.6	2.68	2.75
579	268	2.75	2.83	2.9	2.98	3.05	3.13	3.2	3.28	3.35	3.42	3.49
580	343	3.50	3.58	3.65	3.73	3.8	3.88	3.95	4.03	4.1	4.18	4.25
581	418	4.25	4.33	4.4	4.48	4.55	4.62	4.69	4.77	4.85	4.92	4.99
582	492	5.0	5.07	5.14	5.21	5.28	5.35	5.42	5.49	5.56	5.63	5.7
583	567	5.74	5.81	5.89	5.97	6.04	6.12	6.19	6.26	6.34	6.41	6.48
584	641	6.49	6.56	6.64	6.71	6.78	6.86	6.93	7.01	7.08	7.15	7.22
585	716	7.23	7.29	7.35	7.41	7.47	7.53	7.6	7.68	7.75	7.82	7.89
586	789	8.05	8.12	8.19	8.27	8.34	8.42	8.49	8.56	8.63	8.7	8.77
587	871	8.78	8.85	8.93	9.01	9.08	9.16	9.23	9.3	9.37	9.44	9.51
588	945	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.3
589	77	0.12	0.19	0.26	0.34	0.41	0.48	0.56	0.63	0.7	0.78	0.85
590	085	0.93	1.00	1.07	1.15	1.22	1.29	1.37	1.44	1.51	1.58	1.65
591	159	1.06	1.13	1.21	1.28	1.35	1.42	1.49	1.57	1.64	1.71	1.78
592	232	1.40	1.47	1.54	1.61	1.68	1.75	1.82	1.89	1.96	2.03	2.1
593	305	1.87	1.97	2.07	2.17	2.27	2.37	2.47	2.57	2.67	2.77	2.87
594	379	2.36	2.33	2.32	2.31	2.3	2.29	2.27	2.25	2.23	2.21	2.19
595	452	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6
596	532	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6
597	605	6.12	6.19	6.27	6.34	6.41	6.48	6.55	6.62	6.69	6.76	6.83
598	677	6.65	6.82	6.99	7.16	7.34	7.51	7.68	7.85	8.02	8.19	8.36
599	743	7.67	7.72	7.78	7.84	7.91	7.98	8.05	8.12	8.19	8.26	8.33
600	—	815	822	830	837	844	851	859	866	873	880	887
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional part

LOGARITHMS OF NUMBERS.

600 - 650

LOGARITHMS OF NUMBERS

650 — 700

N. L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
650	291	298	305	311	318	325	331	338	345	351	
651	296	303	310	317	324	331	338	345	352	359	
652	298	305	312	319	326	333	340	347	354	361	
653	303	310	317	324	331	338	345	352	359	366	
654	305	312	319	326	333	340	347	354	361	368	
655	304	311	318	325	332	339	346	353	360	367	
656	300	307	314	321	328	335	342	349	356	363	
657	297	304	311	318	325	332	339	346	353	360	
658	293	300	307	314	321	328	335	342	349	356	
659	298	305	312	319	326	333	340	347	354	361	
660	302	309	316	323	330	337	344	351	358	365	
661	304	311	318	325	332	339	346	353	360	367	
662	306	313	320	327	334	341	348	355	362	369	
663	305	312	319	326	333	340	347	354	361	368	
664	217	223	230	236	243	249	256	263	269	276	
665	282	289	295	302	308	315	321	328	334	341	
666	287	294	301	308	315	322	329	336	343	350	
667	284	291	298	305	312	319	326	333	340	347	
668	413	418	423	428	433	445	452	458	465	471	
669	478	484	491	497	504	510	517	523	530	536	
670	607	614	620	627	633	640	646	653	659	666	
671	602	609	616	623	629	636	643	650	657	664	
672	605	612	619	626	633	640	647	654	661	668	
673	607	614	621	628	635	642	649	656	663	670	
674	866	872	878	885	892	898	905	911	918	924	
675	543	549	556	562	569	575	582	588	595	601	
676	995	997	993	980	966	943	919	975	982	988	
677	83	95	101	108	114	120	127	133	139	145	
678	123	129	136	142	149	155	161	168	174	181	
679	187	193	200	206	213	219	225	232	238	245	
680	251	257	264	270	276	283	289	295	302	308	
681	315	321	327	334	340	347	353	359	366	372	
682	365	371	378	385	391	398	404	410	417	423	
683	376	382	389	395	401	407	414	420	426	432	
684	506	512	518	523	531	537	544	550	556	563	
685	569	575	582	588	594	601	607	613	620	626	
686	632	639	646	653	658	664	670	677	683	689	
687	769	762	778	775	781	787	794	790	796	793	
688	822	828	835	841	847	853	860	866	872	879	
689	885	891	887	894	910	916	923	929	936	942	
690	948	954	960	967	973	979	985	992	998	1004	
691	011	017	023	029	035	042	048	055	061	067	
692	013	019	026	032	038	045	052	059	065	071	
693	116	122	128	134	140	147	153	160	166	172	
694	193	198	205	211	217	223	230	236	242	248	
695	261	267	273	280	286	292	298	305	311	317	
696	333	339	346	352	358	364	371	378	385	392	
697	392	398	404	410	417	423	429	435	442	448	
698	448	454	460	465	471	479	485	491	497	504	
699	510	516	522	528	535	541	547	553	559	566	
700	0	1	2	3	4	5	6	7	8	9	Proportional parts
N. L.	0	1	2	3	4	5	6	7	8	9	

LOGARITHMS OF NUMBERS

1001

LOGARITHMS OF NUMBERS.

750 — 800

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional part
750	87	505	512	518	523	529	535	541	547	553	559	
751	564	570	576	581	587	593	599	604	610	616	622	
752	622	628	633	639	645	651	657	663	669	675	681	
753	679	685	691	697	703	708	714	720	726	731	737	
754	737	743	749	754	760	766	772	777	783	789	795	
755	795	800	806	812	818	823	829	835	841	846	852	
756	853	859	864	869	875	881	887	892	898	904	909	
757	910	916	921	927	933	939	945	951	955	961	966	
758	967	973	978	984	990	996	1001	1006	1011	1016	1021	
759	88	024	030	036	041	047	053	058	064	070	076	
760	081	087	093	098	104	110	116	121	127	133	139	
761	138	144	150	156	161	167	173	178	184	190	196	
762	195	201	207	213	218	224	230	236	241	247	253	
763	252	258	264	270	275	281	287	292	298	304	310	
764	309	315	321	326	332	338	343	349	355	360	365	
765	366	372	378	383	389	395	400	406	412	417	423	
766	423	429	434	440	446	452	458	463	468	474	480	
767	480	485	491	497	503	509	515	520	526	532	538	
768	536	542	547	553	559	564	570	576	582	588	594	
769	593	598	604	610	615	621	627	632	638	643	649	
770	649	655	660	666	672	677	683	689	694	700	706	
771	705	711	717	722	728	734	739	745	751	757	763	
772	772	778	784	790	796	802	807	812	817	823	829	
773	824	830	835	840	846	852	857	863	868	874	880	
774	874	880	885	891	897	902	908	913	919	925	931	
775	930	936	941	947	953	958	964	970	976	981	987	
776	986	992	997	1003	1009	1014	1019	1025	1030	1035	1040	
777	1042	1048	1053	1059	1064	1069	1074	1079	1084	1089	1094	
778	109	104	109	115	120	126	131	137	143	148	154	
779	154	159	165	170	176	182	187	193	198	204	210	
780	209	215	221	226	232	237	243	248	254	260	265	
781	265	271	277	282	287	293	299	304	310	315	321	
782	321	327	332	337	343	348	354	360	365	371	376	
783	378	384	389	395	401	406	412	417	423	429	435	
784	432	437	443	448	454	459	465	471	476	481	486	
785	487	492	498	504	509	515	520	525	531	537	543	
786	542	548	553	559	564	575	581	587	592	598	603	
787	597	603	609	614	620	625	631	636	642	647	653	
788	653	658	664	669	675	680	686	691	697	702	707	
789	713	719	724	729	735	741	746	752	757	763	768	
790	733	738	744	749	755	760	766	771	776	782	787	
791	780	785	790	795	800	805	810	815	820	825	830	
792	823	828	834	839	844	849	855	860	865	870	875	
793	873	878	883	888	893	898	903	908	913	918	923	
794	922	927	932	937	942	947	952	957	962	967	972	
795	93	037	042	048	053	059	064	069	075	080	086	
796	151	157	162	168	173	179	184	189	195	200	206	
797	200	206	211	217	222	227	233	238	244	249	254	
798	255	260	266	271	276	282	287	293	298	304	309	
799	309	314	320	325	331	336	342	347	352	358	363	
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional part

Proportional part

LOGARITHMS OF NUMBERS

800 — 850

LOGARITHMS OF NUMBERS

850 — 900

N.	1.	0	1	2	3	4	5	6	7	8	9	Proportional parts
850	92	592	447	652	652	652	957	973	978	983	988	
850	93	593	448	653	653	653	958	973	978	983	988	
850	94	594	449	654	654	654	958	973	978	983	988	
853	95	100	105	105	105	105	104	104	104	104	104	
853	146	151	156	161	161	161	165	165	165	165	165	
855	197	202	207	212	217	222	227	232	237	242	247	6
856	247	252	258	263	268	273	278	283	288	293	298	
857	298	303	308	313	318	323	328	333	338	343	348	
859	349	354	359	364	369	374	379	384	389	394	399	
859	389	404	409	414	420	425	430	435	440	445	450	
860	450	455	460	465	470	475	480	485	490	495	500	
861	500	505	510	515	520	525	530	535	540	545	550	
862	551	556	561	566	571	576	581	586	591	596	601	
863	601	606	611	616	621	626	631	636	641	646	651	
864	651	656	661	666	671	676	681	686	691	696	701	
865	702	707	712	717	722	727	732	737	742	747	752	
867	802	807	812	817	822	827	832	837	842	847	852	
868	852	857	862	867	872	877	882	887	892	897	902	
869	902	907	912	917	922	927	932	937	942	947	952	
870	952	957	962	967	972	977	982	987	992	997	1002	5
871	962	967	972	977	982	987	992	997	1002	1007	1012	
872	002	007	012	017	022	027	032	037	042	047	052	
873	101	106	111	116	121	126	131	136	141	146	151	
874	151	156	161	166	171	176	181	186	191	196	201	
875	201	206	211	216	221	226	231	236	240	245	250	
876	250	255	260	265	270	275	280	285	290	295	300	
877	300	305	310	315	320	325	330	335	340	345	350	
878	350	354	359	364	369	374	379	384	389	394	399	
879	399	404	409	414	419	424	429	434	438	443	448	
880	448	453	458	463	468	473	478	483	488	493	498	
882	547	552	557	562	567	572	577	582	587	592	597	
883	596	601	606	611	616	621	626	631	636	640	645	
884	645	650	655	660	665	670	675	680	685	689	694	
885	694	699	704	709	714	719	724	729	734	738	743	
885	743	748	753	758	763	768	773	778	783	787	792	
887	807	812	817	822	827	832	837	842	847	852	857	
889	851	856	861	866	871	876	881	886	891	896	901	
890	893	898	903	908	913	918	923	928	933	938	943	
890	939	944	949	954	959	964	969	974	979	984	989	
891	988	993	998	1002	1007	1012	1017	1022	1027	1032	1037	
892	003	004	006	005	001	005	001	005	001	005	001	
893	134	139	143	148	153	158	163	168	173	177	181	
894	376	381	386	391	396	399	404	409	414	419	424	
895	396	398	400	395	393	395	397	399	401	403	405	
896	424	429	434	439	444	448	453	458	463	468	473	
N. 1.	0	1	2	3	4	5	6	7	8	9	Proportional parts	

4

5

6

7

8

9

Proportional parts

LOGARITHMS OF NUMBERS

900 — 950

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
900	95.424	429	434	439	444	448	453	458	463	468	473	418
901	95.427	477	482	487	492	497	501	506	511	516	521	416
902	95.430	525	530	535	540	545	550	555	559	564	569	407
903	95.433	573	578	583	588	593	598	603	607	612	617	407
904	95.437	620	631	636	641	646	651	656	661	666	671	407
905	95.440	665	674	679	684	689	694	698	703	708	713	407
906	95.443	713	718	722	727	732	737	742	746	751	756	407
907	95.447	761	766	770	775	780	785	790	794	799	804	407
908	95.450	813	818	823	828	832	837	842	847	852	857	407
909	95.453	861	866	871	875	880	885	890	895	899	904	407
910	95.457	914	918	923	928	933	938	942	947	952	957	407
911	95.460	961	966	971	976	981	986	990	995	999	1004	407
912	95.463	999	1004	1009	1014	1019	1024	1029	1034	1039	1044	407
913	95.467	105	106	107	108	109	110	111	112	113	114	407
914	95.470	104	105	106	107	108	109	110	111	112	113	407
915	95.473	152	153	155	156	158	160	162	164	166	168	407
916	95.476	190	191	193	195	196	198	200	201	203	205	407
917	95.479	237	238	242	244	246	250	252	256	258	262	407
918	95.482	284	289	294	298	303	308	313	317	321	325	407
919	95.485	332	336	341	346	350	355	360	365	369	374	407
920	95.487	379	384	388	393	398	402	407	412	417	421	407
921	95.490	426	431	435	440	445	450	454	459	464	468	407
922	95.493	473	478	483	487	492	497	501	506	511	515	407
923	95.496	520	525	530	534	539	544	549	553	558	562	407
924	95.499	567	572	577	581	586	591	595	600	605	609	407
925	95.502	614	619	624	628	633	638	642	647	652	656	407
926	95.505	661	666	670	675	680	685	690	694	699	703	407
927	95.507	708	713	717	722	727	731	736	741	745	750	407
928	95.510	755	759	764	769	774	778	783	788	792	797	407
929	95.513	806	810	811	816	820	825	830	834	839	844	407
930	95.516	853	858	862	867	872	876	881	886	890	894	407
931	95.519	900	904	909	914	917	923	928	932	937	941	407
932	95.522	946	950	955	960	965	970	974	979	984	988	407
933	95.525	983	987	991	995	999	1003	1007	1011	1015	1019	407
934	95.528	1030	1034	1037	1041	1045	1049	1053	1057	1061	1065	407
935	95.531	1077	1081	1085	1089	1093	1097	1101	1105	1109	1113	407
936	95.534	1128	1132	1137	1142	1146	1151	1155	1160	1165	1169	407
937	95.537	1174	1179	1183	1188	1192	1197	1202	1206	1211	1216	407
938	95.540	220	225	230	234	238	243	248	253	257	262	407
939	95.543	267	271	275	280	284	289	294	299	304	308	407
940	95.546	313	317	322	327	331	336	340	345	350	354	407
941	95.549	358	363	368	373	377	382	387	391	396	400	407
942	95.552	410	414	419	424	428	433	437	442	447	452	407
943	95.555	455	460	465	470	474	479	483	488	493	498	407
944	95.557	502	506	511	516	520	525	530	534	539	543	407
945	95.560	553	558	562	566	571	575	580	585	590	595	407
946	95.563	604	609	614	619	624	629	634	639	644	649	407
947	95.566	655	660	664	669	673	678	683	687	692	697	407
948	95.569	695	699	703	707	711	715	719	723	727	731	407
949	95.572	731	736	740	745	749	754	759	763	768	772	407
950	95.575	777	782	786	791	795	800	804	809	813	817	407
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

LOGARITHMS OF NUMBERS

950 — 1000

N.	1.	0	1	2	3	4	5	6	7	8	9	Proportional parts
950	97	772	777	782	786	791	795	800	804	809	813	
951	818	823	827	832	836	841	845	850	855	859	863	
952	864	868	873	877	882	886	891	895	900	905	909	
953	909	914	918	923	928	932	937	941	946	950	955	
954	953	958	964	968	973	978	982	987	991	996	999	
955	99	000	005	009	014	019	023	028	032	037	041	1
956	046	050	055	059	064	068	073	078	082	087	091	0.5
957	091	096	100	105	109	114	118	123	127	132	137	1.9
958	137	141	146	150	155	159	164	168	173	177	182	1.3
959	182	186	191	195	200	204	209	214	218	223	227	1.7
960	227	232	236	241	245	250	254	259	263	268	272	5
961	272	277	281	286	290	294	299	304	308	313	318	1
962	318	322	327	331	336	340	345	349	354	358	363	2
963	363	367	372	376	381	385	390	394	398	403	408	1.5
964	408	412	417	421	426	430	435	439	444	448	453	4.0
965	453	457	462	466	471	475	480	485	490	495	500	5.3
966	498	502	507	511	516	520	525	530	535	538	543	6.0
967	543	547	552	556	561	565	570	574	579	583	588	7.5
968	588	592	597	601	605	610	614	619	623	628	633	8.2
969	632	637	641	646	650	655	659	664	668	673	678	4.5
970	677	682	686	691	695	700	704	709	713	717	721	
971	722	726	731	735	740	744	749	753	758	762	767	
972	767	771	776	780	784	789	793	798	802	807	811	
973	811	816	820	825	829	834	838	843	847	851	855	
974	856	860	865	869	874	878	883	887	892	896	900	
975	900	905	909	914	918	923	927	932	936	941	945	
976	945	949	954	958	963	968	972	977	981	985	989	
977	989	994	998	003	007	012	016	020	024	028	032	
978	034	038	043	047	052	057	061	065	069	074	078	
979	078	083	087	092	096	100	105	109	114	118	122	
980	123	127	131	136	140	145	149	154	158	162	167	
981	167	171	176	180	185	189	193	198	202	207	212	
982	211	216	220	224	229	233	238	242	247	251	256	
983	260	264	269	273	277	282	286	291	295	299	303	
984	300	304	308	313	317	322	326	330	335	339	343	
985	344	348	352	357	361	366	370	374	379	383	387	
986	386	390	395	400	405	410	415	420	425	430	435	
987	436	439	445	450	456	461	467	473	479	485	491	
988	476	480	484	489	493	498	502	506	511	515	521	
989	524	528	533	537	542	546	550	555	559	563	567	
990	564	568	572	577	581	585	590	594	599	603	607	
991	607	612	616	621	626	629	634	638	642	647	651	
992	651	656	660	664	669	673	677	682	686	691	695	
993	695	699	704	708	712	717	721	726	730	734	738	
994	739	743	747	752	756	760	765	769	774	778	782	
995	782	787	791	795	800	804	808	813	817	821	825	
996	826	830	835	839	843	848	852	856	861	865	869	
997	866	870	874	878	882	886	890	894	898	902	906	
998	893	897	901	905	910	915	919	923	927	931	935	
999	937	941	945	949	953	957	961	965	969	973	977	
1000	00	000	004	009	013	017	022	026	030	035	039	Proportional parts
N.	L.	0	1	2	3	4	5	6	7	8	9	

INTERNATIONAL ATOMIC WEIGHTS 1941

	Sym- bol	Atomic No.	Weight		Sym- bol	Atomic No.	Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

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